INSTITUTE OF METALS DIVISION

1945

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(INCORPORATED)

and Petroleum

Volume 161

INSTITUTE OF METALS DIVISION

1945

TECHNICAL PAPERS AND DISCUSSIONS AND SYMPOSIA PRESENTED
BEFORE THE DIVISION AT MEETINGS HELD AT NEW YORK,
FEBRUARY 20–24, 1944 AND AT CLEVELAND, OCTOBER 16–18, 1944;
ALSO PAPERS SCHEDULED FOR THE MEETING AT NEW YORK,
FEBRUARY 19–22, 1945, WHICH WAS CANCELED

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Notice

This volume is the nineteenth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the New York Meeting, Feb. 20–24, 1944, and the Cleveland Meeting, Oct. 16–18, 1944; also papers scheduled for the New York Meeting, Feb. 19–22, 1945, which was canceled. The complete list of publications and proceedings, including the present volume, is as follows:

1908–1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.

1912–1916 *Transactions* of the American Institute of Metals, Vols. 6–10.

1917–1918 *Journal* of the American Institute of Metals, Vols. 11–12.

1919–1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927–1928 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A.I.M.E. TRANSACTIONS.

1929–1945 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 83, 89, 93, 99, 104, 111, 117, 122, 124, 128, 133, 137, 143, 147, 152, 156 and 161, Institute of Metals Division.

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FOREWORD

The impact of war has caused marked changes in the educational functions of the American Institute of Mining and Metallurgical Engineers in the past year. Extensive program arrangements had been made for the February 1945 meeting in New York, but in order to assist in avoiding congestion of railroad and hotel facilities, the meeting was canceled by the Institute. Moreover, because of secrecy rulings of the armed forces, much of the war work of the membership of the Institute has been of a restricted nature and cannot be reported at this time. Nevertheless, the Institute of Metals Division may take justifiable pride in the present volume of the TRANSACTIONS, which is by far the largest it has ever published and which contains a well-rounded collection of papers of excellent quality. The volume represents the unstinted efforts of the Division's Programs Committee with A. A. Smith as Chairman, and the Division's Publications Committee under the Chairmanship of E. A. Anderson. On behalf of the Institute, I express most grateful appreciation.

The 1945 volume includes the papers submitted at the powder metallurgy conference and the continuous casting symposium in New York in February 1944; the papers, including those for the creep symposium, presented at Cleveland in October 1944, and some of the papers that were to have been presented at the canceled New York meeting of February 1945.

The more fundamental papers concern physical metallurgy, copper and copper-rich alloys, magnesium alloys, and miscellaneous metals and alloys. The symposia on continuous casting and on creep are the second and third, respectively, of a long-term program, while the powder metallurgy conference represents the Division's cognizance of the increasing importance of that field of metallurgy. The quality standards of these papers have been maintained at the previous high level set by the Division, and it is believed that a good balance has been struck between the more fundamental papers and those containing information more readily applicable to metals technology.

Special mention must be made of the Institute of Metals Division Lecture, "A New Microscopy and its Potentialities," by Charles S. Barrett. The lecture, which was prepared for the February meeting in New York, is included at the beginning of this volume. From a distinguished author, it is a major contribution to physical metallurgy, and should prove to be a stimulus to other investigators.

Acknowledgment has already been made of the work of two of the committees. It is with the greatest personal pleasure that I thank now the Chairmen and members of the other committees of the Division, who, through their able cooperation, have greatly smoothed my path as Division Chairman. Finally, I wish to acknowledge the continuance of the excellent work of the Secretary of the Division, Frank T. Sisco, and of the Secretary of the Institute's Papers and Publications Committee, E. J. Kennedy, Jr.

Earle E. Schumacher, *Chairman,*
Institute of Metals Division.

Murray Hill, New Jersey,
July 1, 1945.

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ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February. There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmanstätten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. TRANSACTIONS (1931) **93**, 78–110.

1935 R. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. TRANSACTIONS (1934) **111**, 264–292.

1936 Cyril S. Smith and W. Earl Lindlief: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. TRANSACTIONS (1933) **104**, 69–105.

1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. TRANSACTIONS (1934) **111**, 94–112.

1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. TRANSACTIONS (1936) **122**, 284–293.

1939 Frederick N. Rhines and Robert F. Mehl: Rates of Diffusion in the Alpha Solid Solutions of Copper. TRANSACTIONS (1938) **128**, 185–221.

1940 Alden B. Greninger: Martensite Transformation in Beta Copper-aluminum Alloys. TRANSACTIONS (1939) **133**, 204–221.

1941 S. E. Maddigan and A. I. Blank: Recovery and Recrystallization in Long-time Annealing of 70-30 Brass. TRANSACTIONS (1940) **137**, 170–190.

1942 F. N. Rhines: A Metallographic Study of Internal Oxidation in the Alpha Solid Solutions of Copper. TRANSACTIONS (1940) **137**, 246–288.

1943 J. D. Hanawalt, C. E. Nelson and J. A. Peloubet: Corrosion Studies of Magnesium and Its Alloys. TRANSACTIONS (1942) **147**, 273–298.

1944 A. H. Geisler, C. S. Barrett and R. F. Mehl: Aging in the Solid Solution of Silver in Aluminum. TRANSACTIONS (1943) **152**, 182–200.

1945 William M. Baldwin, Jr.: Effect of Rolling on the Crystallography, Metallography, and Physical Properties of Copper Strip. METALS TECHNOLOGY, April 1942.

THE INSTITUTE OF METALS LECTURE

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
1923 Solid Solution. By Walter Rosenhain.
1924 The Trend in the Science of Metals. By Zay Jeffries.
1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
1927 Growth of Metallic Crystals. By Cecil H. Desch.
1928 Twinning in Metals. By C. H. Mathewson.
1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
1932 The Age-hardening of Metals. By Paul D. Merica.
1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
1935 Gases in Metals. By C. A. Edwards.
1936 Diffusion in Solid Metals. By Robert F. Mehl.
1937 Refractories. By R. S. Hutton.
1938 The Nature of Metals as Shown by Their Properties under Pressure. By P. W. Bridgman.
1939 The Creep of Metals. By D. Hanson.
1940 Acceleration of Rate of Corrosion by High Constant Stresses. By Edgar H. Dix, Jr.
1941 Some Fundamentals of the Flow and Rupture of Metals. By George Sachs.
1942 Notes on the History, Manufacture, and Properties of Wrought Brass. By Wm. Reuben Webster.
1943 Applications of the Electron Microscope in Metallurgy. By V. K. Zworykin.
1944 Some Problems in Organizing Industrial Research. By W. M. Peirce.
1945 A New Microscopy and Its Potentialities. By Charles S. Barrett.

TECHNICAL PAPERS
AND
DISCUSSIONS

Charles S. Barrett

Institute of Metals Division Lecturer, 1945

A New Microscopy and Its Potentialities

By Charles S. Barrett,* Member A.I.M.E.

(Institute of Metals Division Lecture†)

There is a road into the microscopic realm that has remained untraveled through all these years of intense activity with high-power optical and electron microscopy. The road is worthy of careful scouting by metallurgists and other investigators, for it leads into relatively new country and it makes some areas accessible that heretofore could be reached only by very indirect paths or by the use of imagination. And when the road passes through familiar territory it frequently permits a new view of commonplace things that should prove of value from time to time.

An accepted way to interest people in new sights such as this is to present an illustrated travelogue. This I propose to do, using many pictures taken in my recent exploration of this road. In the manner of travelogues, I shall touch briefly upon a large number of different subjects in physical metallurgy and shall attempt to give an exhaustive treatment of none, for the objective is to provide a means for further research, to interest others in it, and to indicate what appears at the moment to be profitable directions for it to take.

The method I shall present involves X-rays, but does not make use of the usual accompaniments of X-ray research such as reciprocal lattices, Fourier series, or the stereographic projection. The method is so simple in its fundamentals that it could have been developed 20 years ago, or perhaps even 30 years ago.

It is well to have a destination for our travels, so that when we are through we shall have explored some region of importance, despite our preoccupation with the novel means of transportation and our interest in the sights to be seen along the way. So let us name the Cold-worked State as our destination, and make side trips into the territories known as Recovery, Recrystallization, and Precipitation-hardening. A great many investigations have been made of the nature of cold-worked metal, and a great variety of methods used, many of which are indirect, such as X-ray line intensities, X-ray line widths, calorimetric measurements, and magnetic measurements. Since comprehensive reviews of these investigations have been published in recent years, they need not be discussed here.

The investigations that were the direct forerunners of the present work should be first mentioned. In 1931 I became interested in the structure of individual spots in X-ray diffraction patterns.[1] When a crystal is placed in the narrow pencil of X-rays in a Laue camera, the spots recorded on the film are not always uniformly black, but may have an internal structure. The meaning of this may be understood from Fig. 1, which represents a narrow beam containing X-rays of many wave lengths ("general radiation") penetrating a crystal in the direction of the arrow and forming a pattern on the vertical film at the right.

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* Professor Metallurgical Engineering and Member of Staff of Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

† Twenty-fourth Annual Lecture. Scheduled for presentation at the New York Meeting, February 1945, which was cancelled. Issued as T. P. 1865 in Metals Technology, April 1945.

[1] References are at the end of the paper.

In the sketch two Laue spots are shown above the central ray and two below. Each spot is formed by reflections from the front and the back surfaces of the crystal, as indicated by the broken lines, and also from interior points in the crystal. Because reflecting planes of atoms are parallel throughout the interior of the crystal, it follows that the reflected rays forming a single spot are all parallel, hence that each point in a spot corresponds to a certain small volume in the reflecting crystal. The variation of intensity from point to point in the spot records the intensity of reflection from the corresponding points in the crystal. For example, the front and back surfaces of a quartz crystal that had been ground with abrasive produced stronger reflections than the interior, as indicated in the drawing. It was found that the spots record the distribution of *inhomogeneous strain* throughout the interior of the crystal, these strains acting to alter the reflecting power. The spots record not only the plastic strains introduced by grinding the surface but also those that exist as natural imperfections in the crystal, which were found to be severe in some natural rock-salt crystals, and those produced by stresses within the elastic limit. A conclusive proof that elastic strains could alter the reflecting power was obtained in collaboration with Dr. Carl E. Howe,[2] by photographing the spots from a quartz crystal while the crystal was undergoing piezoelectric oscillations. The spots have a fine structure of the type illustrated in Fig. 2, a structure that varies from point to point through the crystal and that disappears when the oscillations cease. It is possible, then, to map out the *distribution of strains* over the surface and throughout the interior of a crystal by observing the internal structure of the X-ray reflections.

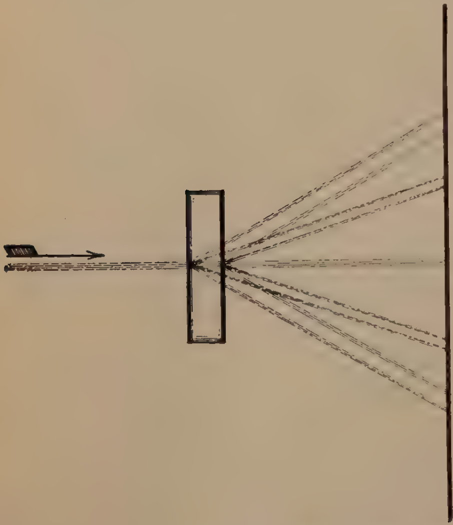

FIG. 1.—THE ORIGIN OF INTERNAL STRUCTURE IN LAUE SPOTS.

Strong reflections from front and back surfaces of a crystal are indicated by broken lines.

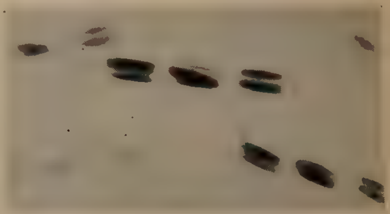

FIG. 2.—LAUE SPOTS FROM OSCILLATING QUARTZ CRYSTAL, SHOWING STRUCTURE PRODUCED BY ELASTIC STRAINS.

Pattern on X-ray film, general radiation; three pinholes in a row; portion of film reproduced natural size.

Simultaneously with this work and entirely independently, very similar experiments were performed in Japan.[3-5] Also, some very closely related experiments were being conducted in Germany by W. Berg,[6,7] who employed X-rays of a single wave length and caused reflection to take place from the cleavage surface of rock-salt crystals. Berg used an X-ray tube at a long distance from the crystal and a photographic plate close to the crystal. An image of the crystal was formed by reflected monochromatic X-rays, the details of the diffracted image from one set of atomic planes furnishing a picture of the point-to-point variation of the reflecting power over the crystal surface. Crystals that had been plastically deformed by cleavage or by compression produced striated images, as if along the slip planes there had occurred a rotation of the crystal lattice during plastic flow.

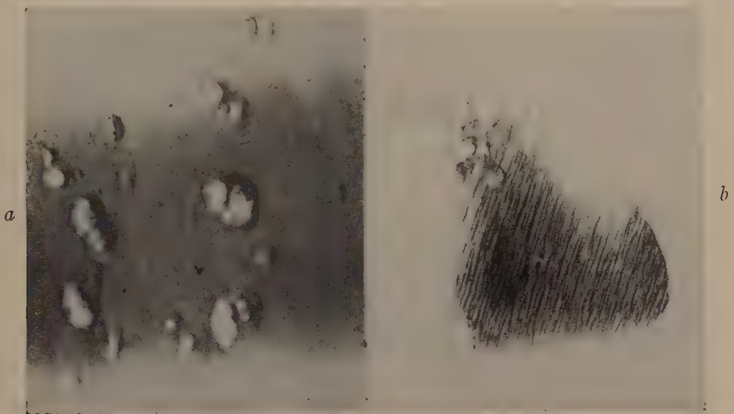

FIG. 3.—INDIVIDUAL X-RAY REFLECTION FROM SILICON FERRITE CRYSTAL. × 10. *a*, electropolished; *b*, same crystal after twisting.

During a period of ten years or more following these experiments, no advances were made in the method and it was not tried on metals, the really fruitful field for it. When Dr. Roger Potvin, of Laval University, Canada, was a guest at Carnegie Institute of Technology recently, I proposed a continuation of these experiments and an attempt to extend them to metallurgical specimens. During Dr. Potvin's visit a number of pictures were made that confirmed the theory that strains along the slip planes of rock salt increase the reflecting power and produce lines in the images. Single crystals of silicon ferrite were then investigated, with most interesting results.

A crystal was tilted until a strong reflection of monochromatic X-rays was seen on a fluorescent screen. The reflection was recorded on an X-ray film placed close to the specimen and the spot produced by the reflected rays was enlarged 10 diameters. When the crystal was undistorted the spot appeared as in Fig. 3 at the left; it was found to consist of a uniform background with occasional white spots. The gray background signifies a uniform reflecting power over the surface of the crystal, and the white spots, not reflecting, are doubtless included grains of a different orientation. After the crystal was bent and straightened by hand the picture at the right of Fig. 3 was obtained, and it was seen that twisting the metal had introduced a striated appearance that had not been present originally. The wealth of detail seen at this magnification suggested that the negatives were worthy of further study and greater magnification.

These experiments conducted with Dr. Potvin brought out the fact that *micrographs* of metals could be prepared by X-ray diffraction; that the micrographs could show changes induced by deformation; that the use of fine-grained photographic emulsions that could stand great enlargement should be tried; and that to get good pictures it is necessary to prepare a crystal surface that is free from scratches and flowed metal, using electrolytic polishing, for example. The summer's work was indeed most encouraging and I wish at this time to express my sincere appreciation to Dr. Potvin for his efforts.

Cameras and Techniques

Let us turn now to the fundamental principles involved, in order to see what conditions should produce the best micrographs. Fig. 4 is a sketch representing the diffraction of beam of X-rays of a single wave length by a small crystal. The beam comes from the left, passes through a slit of width *S* and strikes the crystal at a distance *X* from the slit. As Bragg has shown, a diffracted ray is directed in space as if it were a ray of light reflected from a mirror, the layers of atoms in the crystal acting as the mirror, with the added restriction that a ray must enter the crystal at a definite angle if reflection is to occur. Consequently the incident and reflected rays go in the directions indicated by the large arrows in the sketch; they approach the crystal along a generator of an imaginary cone and leave the crystal along the diametrically opposite generator. The cone stands with its axis perpendicular to the reflecting plane of atoms.* We are concerned with the image the reflected ray makes when it strikes a photographic plate (or film), how to make this image correspond point by point to the surface of the specimen, and how to increase the sharpness of the image so that great enlargement is justified.

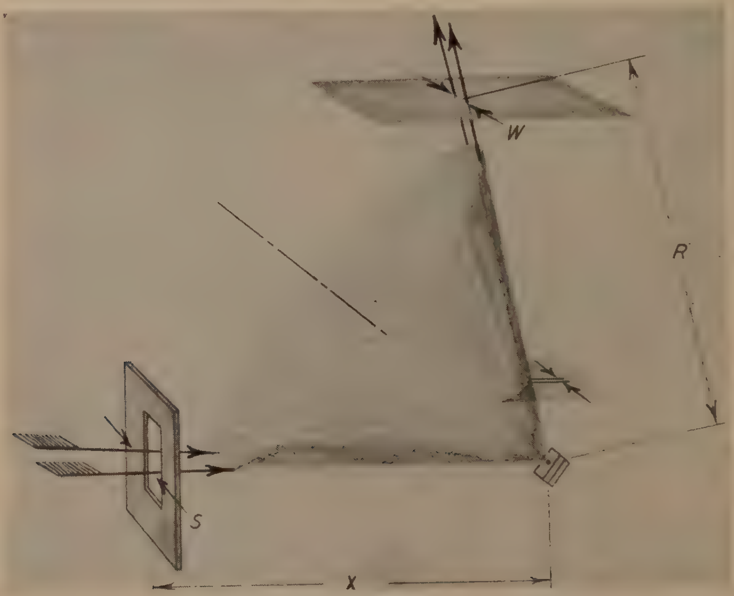

FIG. 4.—REFLECTING CONDITIONS FOR AN ATOMIC PLANE.
Incident and reflected rays are diametrically opposite generators of a cone surrounding the reflecting plane normal.

Suppose, then, we let the sketch represent the reflection of X-rays of a single wave length from one infinitesimal point on the surface of a crystal that is assumed perfect and free from distortion. The image on the photographic plate will be a spot of width *W*, a width that is dependent upon the distance of the plate from the specimen, the distance *R*. The spot width *W* must be made as small as possible if we are seeking the greatest detail in our micrographs, for it limits the resolving power of the method.

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* Note that this cone surrounds the reflecting plane normal, not the direct beam; it is not the cone that produces Debye rings in a powder diffraction camera.

To make W small, we must decrease R, or decrease S, or increase X, since

$$W = \frac{SR}{X}$$

For example, if the photographic plate is moved to the lower position indicated in the sketch, the width will be ⅕ the width W that it has in the upper position. For highest resolution the distance R should be made as small as possible. In practice, the photographic plate is placed in actual contact with some parts of the specimen. In this essential feature the present method differs radically from ordinary practice in X-ray diffraction. It is not at all difficult to make the distance R less than 1/100 the value that is used in present-day X-ray diffraction cameras.

To take a reasonable example, R may be 0.1 mm. and X may be 100 mm. Then if S is 2 mm. the width W is computed to be 0.002 mm. (2 microns) and we might hope to resolve any details on the specimens that are more than 2 microns apart. I have chosen S in this example as 2 mm. because that is about the width of the focal spot in an X-ray tube, so it follows that we do not even need the slit S, and can use the entire beam from the window of the X-ray tube if we wish.

A camera using this principle is illustrated in Fig. 5. The sketch indicates an X-ray beam coming from the left and passing under a metal shelf on which the photographic plate rests, emulsion side down. The crystal fits up against the underside of this plate and is turned into a reflecting position in the beam of X-rays by turning the circles of the mounting. The adjustment of the crystal is made while watching a fluorescent screen that is placed above the crystal. In a darkened room the reflection of the characteristic radiation can be readily seen on the screen if the eye has become accommodated to the dark for 15 to 20 minutes. The room may be left dark during the exposure so that no covering is necessary over the plate, or a cover may be placed over the entire instrument. It is important, of course, to protect the operator from both

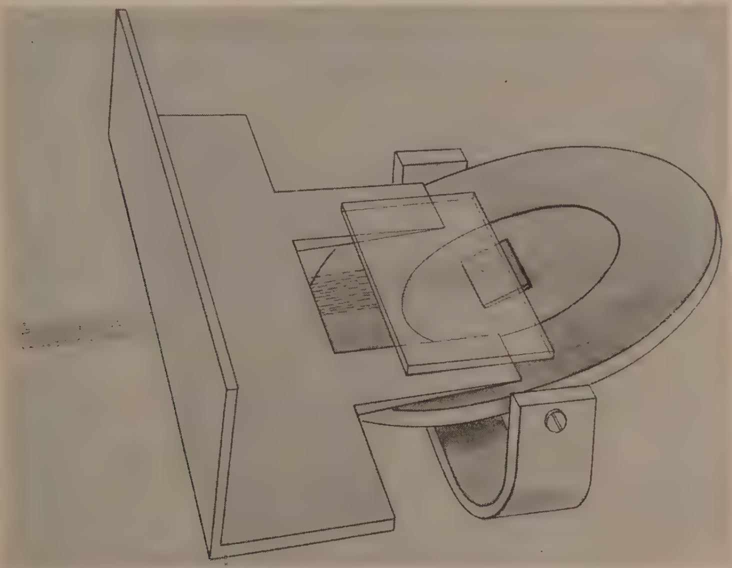


FIG. 5.—X-RAY CAMERA FOR SINGLE CRYSTALS.

the direct and the scattered radiation while adjusting the crystal.

A goniometer arrangement such as this is not necessary if the sample is a powder or a polycrystalline material, for the varying orientations of the grains in the sample will then provide some grains with the proper setting for reflection. The camera may then be reduced to the startling simplicity of Fig. 6. The drawing indicates a cylindrical specimen resting on the emulsion of a photographic plate, and supported on a simple metal housing. The beam of X-rays coming from the left is prevented from darkening the plate by the shielding action of the plate itself, because the rays are unable to penetrate far into the glass, and because the beam is directed slightly upward so as to clear the face of the plate. The L-shaped housing serves to catch the rays that are not stopped by the specimen. Various grains along the front and bottom of the specimen reflect, but the best images are made by the grains that are closest to the plate. A flat specimen serves equally well in this camera, for it can be placed in contact with the plate at the rear and lifted from the plate a millimeter or so in front, in order that the direct beam may reach its underside. This arrangement is shown in the photograph of a camera with plate and specimen attached, Fig. 7. This camera is used with the photographic plate in a vertical position, at right angles to the surface of the target in the X-ray tube.

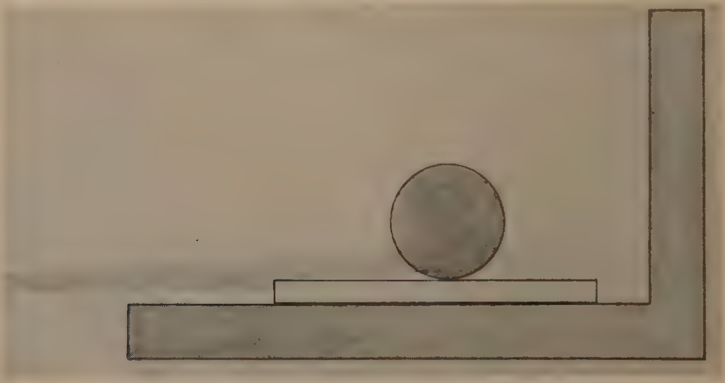


FIG. 6.—CAMERA FOR POLYCRYSTALLINE SPECIMENS.
Cylindrical specimen rests against photographic plate.

a setting that is favorable to sharpness in the images.

Let us now consider the various reflected rays that may be obtained from a specimen. Fig. 8 indicates the angles between the direct beam entering at the left and the reflected rays that may be obtained from the various grains of a polycrystalline specimen, if characteristic radiation from a cobalt target is used, which possesses a strong monochromatic component, and if the specimen is alpha iron or an alloyed ferrite. The most intense and contrasty reflections are those that go out at small angles, while the highest resolution in the photographic image can be expected in an image produced by a ray that is approximately perpendicular to the photographic plate (the plate is indicated just above the specimen); a nearly perpendicular ray, also, will produce an image having the least distortion of shape.

Since crystals send out reflected beams in different directions, overlapping of the images sometimes occurs. To avoid excessive overlapping, it is desirable to have only a single reflection from a crystal strike the plate. Overlapping will be at its worst if one uses general radiation from a tungsten target, which causes reflections in such great numbers that individual images of the grains cannot be seen on the plate. The best conditions will be found when long wave length, monochromatic radiation is used, for then the reflections are few, and, in addition, the penetration into the specimen is small. For clear pictures, it is a good rule that the target in the X-ray tube should have an atomic number equal to or less than the atomic number of the elements in the specimen, for this reduces the fogging caused by fluorescent radiation from the specimen. Targets of chromium, iron, or cobalt are generally suitable. All of the accompanying photographs were made with cobalt targets and without the use of filters.

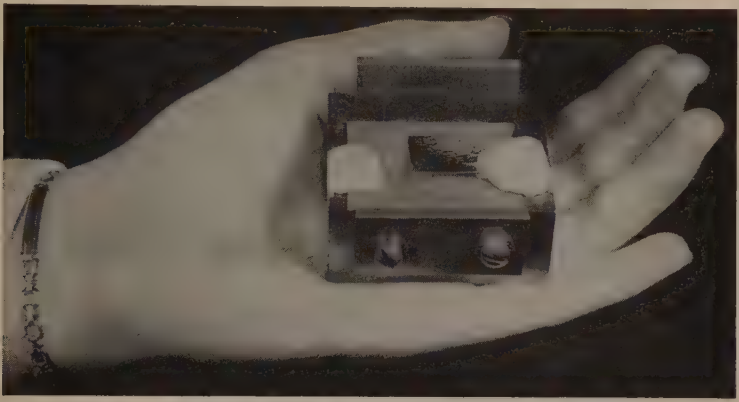


FIG. 7.—CAMERA USED FOR POLYCRYSTALLINE SPECIMENS. Flat specimen and photographic plate in place.

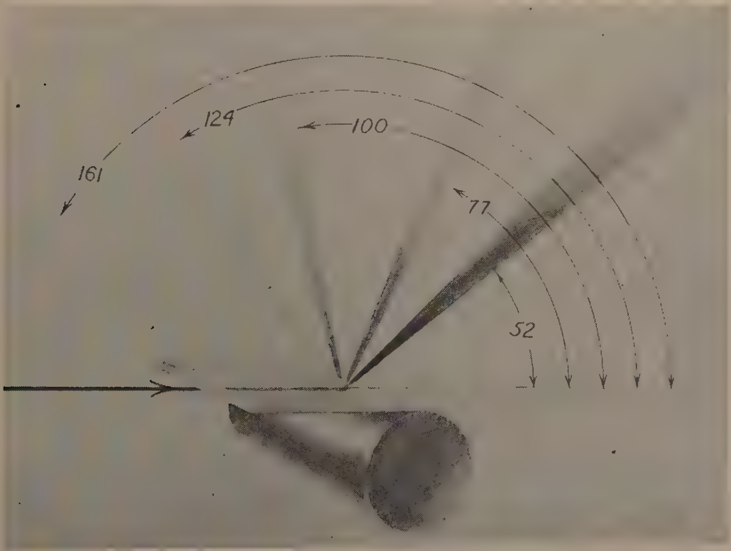


FIG. 8.—POSSIBLE REFLECTIONS FROM IRON USING COBALT CHARACTERISTIC RADIATION. Angles between reflected and incident beams indicated.

The conditions for good images are as follows:

1. A specimen surface undistorted by sawing or polishing.

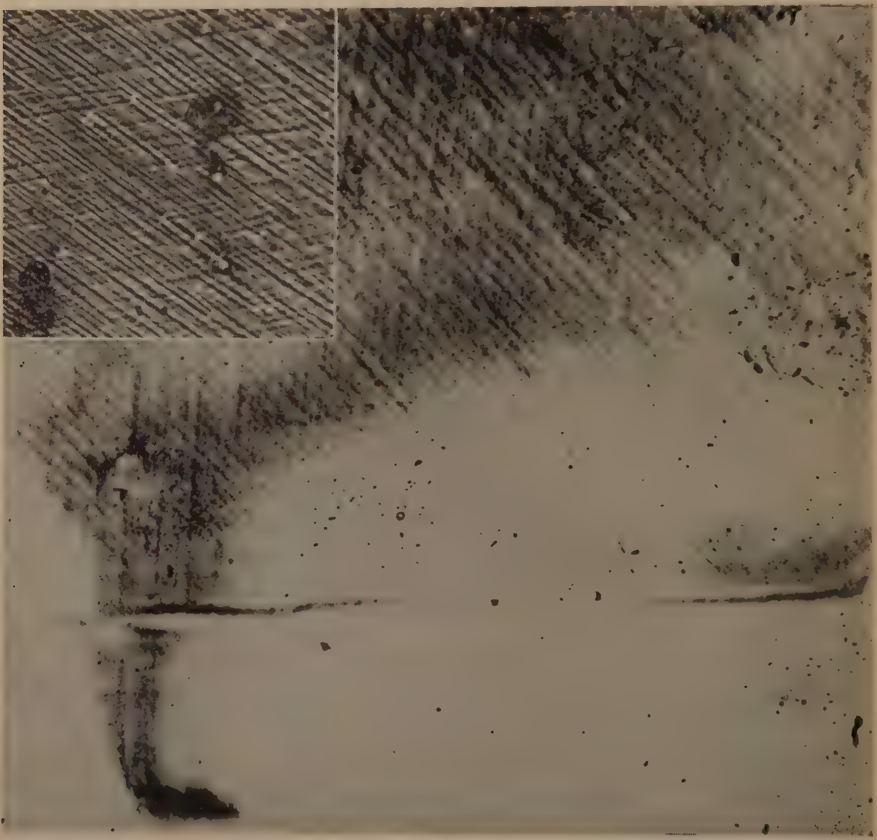


FIG. 9.—X-RAY MICROGRAPH OF SILICON FERRITE CRYSTAL (4 PER CENT SILICON) TWISTED, STRAIGHTENED, ELECTROPOLISHED, SHOWING SLIP LINES. × 100.
548-O spectroscopic plate.
Insert: Optical micrograph of slip lines in a similar crystal. × 100.

2. A minimum distance from specimen to plate.

3. An X-ray tube with target of low atomic number (Cr, Fe, Co) emitting characteristic radiation.

4. A plate shielded from the direct beam.

5. A plate with high resolving power (fine grain).

6. Examination or enlargement of the plate with good lenses, using transmitted light.

Details of the photographic technique used for the accompanying pictures are collected in Appendix I. X-ray film is used only for quick preliminary exposures and low-magnification work; spectroscopic plates are necessary for high resolution and are available with various emulsions that are designed to resolve up to 1000 lines per millimeter. The exposure times for these increase with resolving power from a few minutes up to a maximum of ten or twenty hours for the finest grained plates.

Consider now some examples of what may be accomplished under the conditions that have been mentioned. With a high-resolution plate very close to the specimen the X-ray micrograph reproduced in Fig. 9 was obtained, using the same iron-silicon crystal shown in Fig. 3. The magnification is 100 diameters. Black lines correspond to lines of high reflecting power on the specimen and white areas represent nonreflecting portions of the crystal, just as in the original negative. There are three sets of parallel lines crossing each other, as one would expect if the lines are due to crystallographic slip, for an earlier study of this crystal by Barrett, Ansel and Mehl[8] has shown that slip here is confined to (110) planes and that it produces a network of lines on the surface very similar to this (an ordinary micrograph of another crystal of the same material with similar slip lines is shown in the insert).

The black spots that are so prominent in the white areas represent certain deposits from the Pittsburgh atmosphere, also enlarged 100 diameters. The broad horizontal line is a scratch on the specimen, and the finer diagonal scratch is typical of scratches on the emulsion. These defects are left in the picture to illustrate the precautions necessary; the plates should be rinsed in a jet of water, handled with care to avoid scratches, and dried in a dust-free enclosure.

Fig. 10 shows a portion of the same crystal after a single bend. It gives an indication of the maximum magnification that appears useful at the present time in X-ray micrographs; the magnification is 250 diameters. Lines on the specimen that are separated by 2 to 3 microns (0.002 to 0.003 mm.) are resolved in the picture. Comparing these results with what can be done with the various objectives of an ordinary microscope, one concludes that the resolution in the image is somewhat less than can be obtained with a 16-mm. objective, and perhaps approximates the resolution of a 32-mm. objective.

The "depth of focus" of a camera for the present kind of work is very large, especially when the collimation of the incident beam is high. A curious feature of the method is the tremendous "field of view" that can be recorded on the negative—a field far greater than can be covered by a microscope objective at a magnification of 25 or higher. One can easily make a photograph that would be many square feet in area at 100 diameters.

The condition of the surface with respect to tarnish, rust and finger prints is quite immaterial; one can obtain good pictures from specimens that would be considered entirely worthless for ordinary metallography. On the other hand, these pictures are ruined by a layer of metal disturbed by metallographic polishing when that layer would not be too objectionable to a metallographer using an optical microscope at low magnifications. An excellent procedure, when it can be employed, is to polish the sample by ordinary metallographic methods when the sample is in the cold-worked condition, and then to recrystallize it under conditions that will retain the smooth surface.

Theory of the Strain Markings

As to the important question of the cause of the lines in these pictures, it is not enough to say that they are found in the crystal only after deformation and that they are images of slip lines that appear on the surface as a result of the deformation.

We must first determine whether or not they could be shadow effects on the surface analogous to the optical effects that make slip lines visible in an ordinary microscope. This is certainly not true, for in the particular experiment of Fig. 10*a*, after the crystal had been deformed and before the picture was taken, the crystal was electropolished until the surface contained no geometrical markings, only the irregular ridges shown in the micrograph inserted in the corner of Fig. 10*a*. It must be concluded that since the lines are not produced by shadow effects on the surface, they must

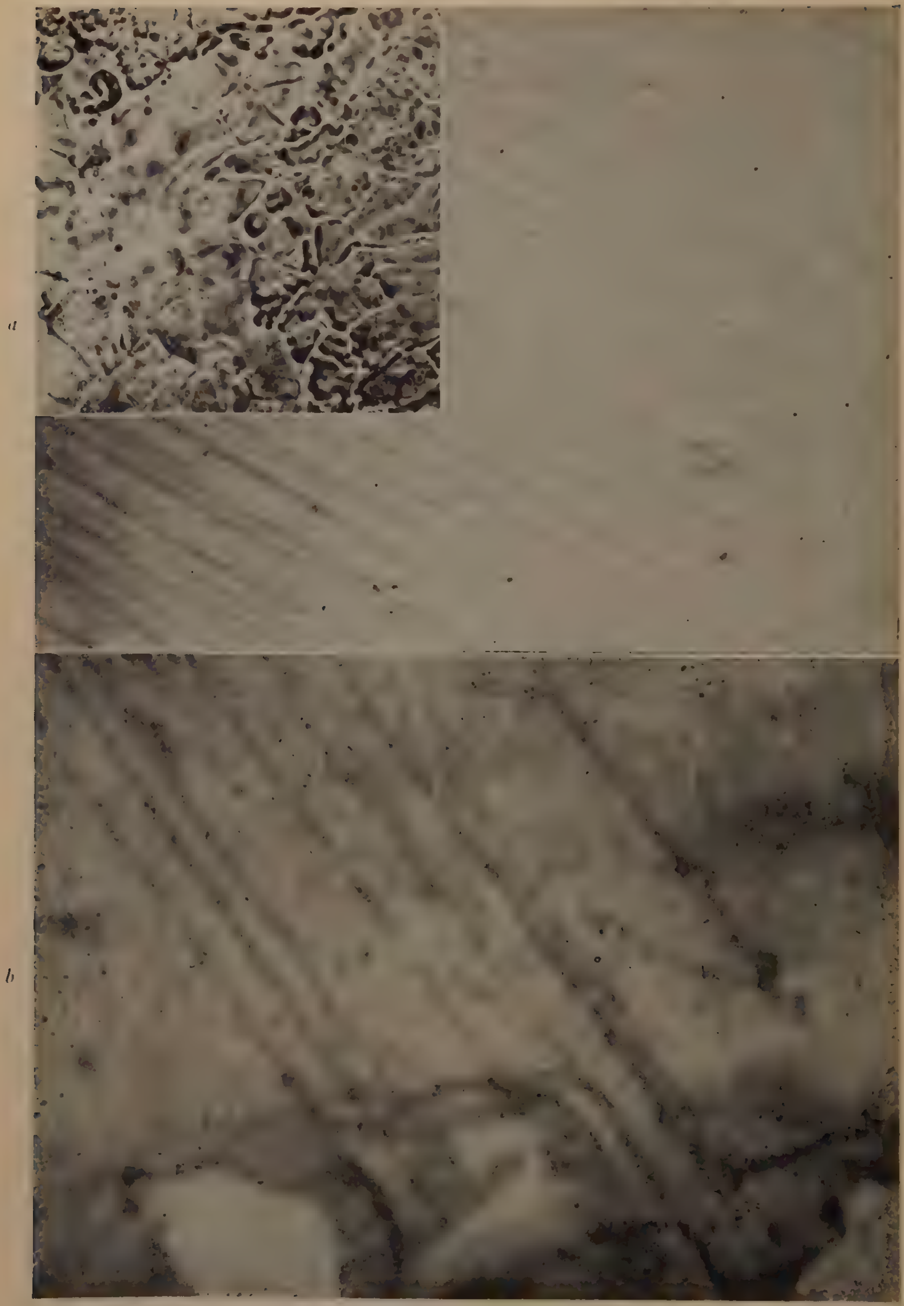


Fig. 10.—Silicon ferrite crystal, × 250.
a. bent, electropolished; insert is optical micrograph of same surface, × 100.
b, slightly bent, not subsequently electropolished (548-ortho spectroscopic plate).

arise from a distorted condition of the crystalline lattice along slip planes in the *interior* of the crystal.

This is a novel situation, for the metallographer knows that slip lines are effaceable—that in ordinary micrography they are removed by polishing and cannot be made visible again by etching—yet in these pictures the lines are clearly visible even after a long series of polishing operations.

We next inquire whether the principal cause of the lines is to be sought in the state of *stress* along the slip lines, or, on the other hand, in the state of *plastic strain*. Fig. 11 and certain other pictures that are discussed later indicate that plastic strain is the primary cause of these lines, at least in metals, and that the plastic strain probably is in the form of a rotation of local regions of the crystal lattice. Fig. 11 is an X-ray micrograph that was made after the specimen had been given an anneal that should have been sufficient to remove stresses; the specimen was a piece of the bent silicon-steel strip used for Fig. 10 and the stress-relieving anneal was ½ hr. at 650°C. The lines survived the annealing treatment. Experiments presented later show that the pictures remain substantially unchanged until the strained material is consumed by the growth of recrystallized grains during annealing, long after one would expect elastic strains to have been removed.

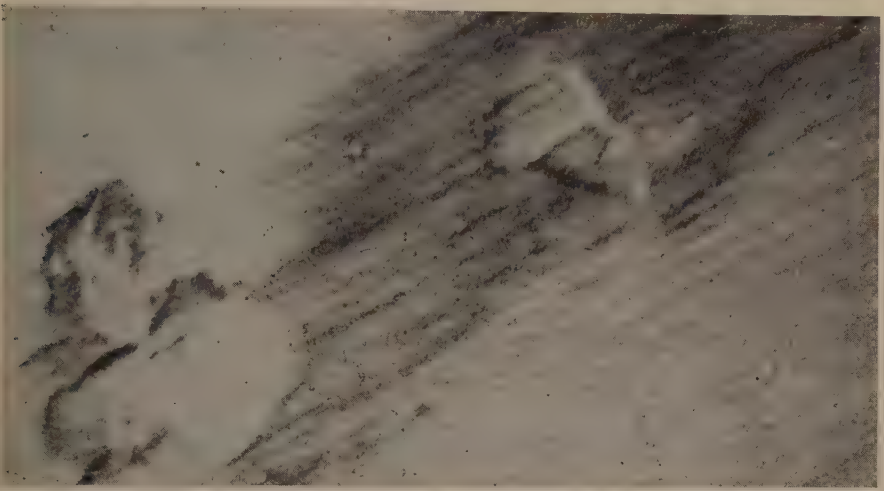


FIG. 11.—SILICON FERRITE CRYSTAL, TWISTED, STRESS-RELIEVED ½ HR. AT 650°C., ELECTROPOLISHED. × 100
548-O spectroscopic plate.

Cold-work must introduce into metals highly localized elastic strains of great intensity, and perhaps these do have some influence on the reflecting power, but on the basis of the data available at this time, it is reasonable to conclude that the major cause of the enhanced reflecting power at the slip lines is plastic strain, not elastic. The pictures, nevertheless, show the *places* where inhomogeneous elastic strains are high in the cold-worked metal, because any mechanism of producing inhomogeneous rotation of the lattice in a microscopic area must involve high residual stresses in the same area.

A simple theory of the lines is presented by means of the sketch in Fig. 12. A crystal in the form of a rectangular block is shown, in which two slip planes are indicated by the dashed lines. One of the atomic planes in the crystal is shown by the surface that is sketched within the block—a surface that is distorted into a wavy contour by the deformation that has occurred at the slip planes. The arrows represent monochromatic X-ray beams reflecting from this wavy surface and making a record of the slip lines on the photographic plate that rests on the top of the block.

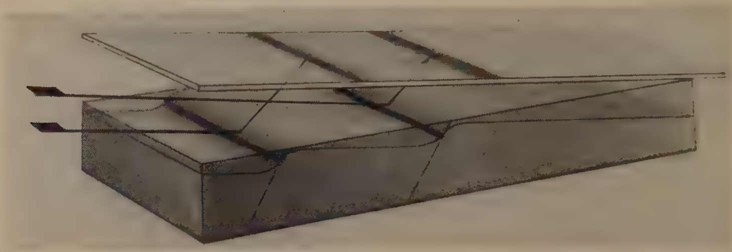


FIG. 12.—SIMPLIFIED THEORY OF ORIGIN OF LINES.
Crystal block below with deformed internal structure; photographic plate above.

This sketch is an oversimplified view of conditions, for it does not explain many facts about the intensities of the lines relative to their background. A better understanding of the cause of the lines may be found by referring to Fig. 13. Consider nonparallel monochromatic rays striking the layers of atoms in the crystal; in the undistorted areas of the crystal, as indicated at the right of this sketch, a single ray from the nonparallel bundle reflects. At distorted regions, however, many of the convergent rays reflect because the different rays find different portions of the crystal in proper reflecting orientation. This is indicated at the left in the sketch. The strained areas, such as those along slip lines, thus make more efficient use of the incident X-ray energy.

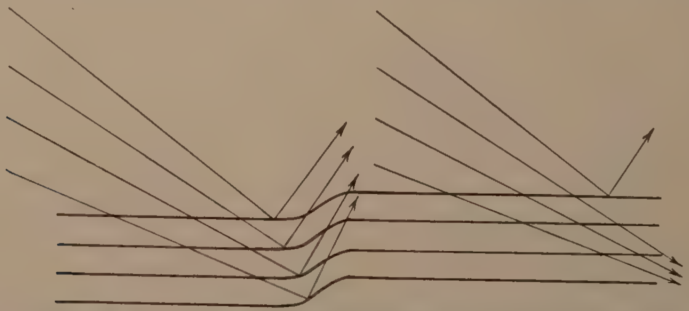
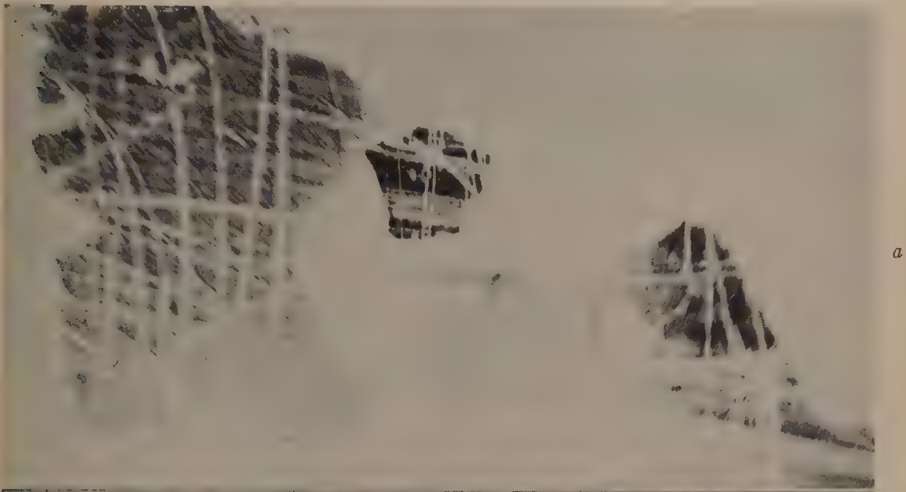


FIG. 13.—ORIGIN OF INTENSIFIED REFLECTION FROM STRAINED REGIONS OF CRYSTAL.

The theory in this form is not complete, for the absorption of the rays has been neglected. Let us therefore consider absorption, remembering that the rate of attenuation of the initial beam in a reflecting crystal may be many times that in a nonreflecting crystal. In an undistorted area of a reflecting crystal all the reflection takes place within a very shallow layer at the surface, particularly when the diffracted ray is one of high intensity, and any ray of the bundle that is being reflected is rapidly reduced in intensity as it enters the crystal; the more rapidly, the more intense the reflection (the higher the "primary extinction"). The nonreflecting rays of the bundle, however, are reduced only by ordinary absorption and in many instances at a much slower rate. Thus some rays of the bundle penetrate, without reflection, through the surface layer and into an underlying region where fragments of the crystal have been strained into a position to reflect. These rays still possess ample power to reflect and add appreciably to the total reflected intensity, with the result that the total reflected intensity is greater from the strained area than from the strain-free area. In other words, strained areas reflect more intensely because a thicker layer of the crystal contributes to the reflected beam and because this thicker layer makes use of a larger fraction of the incident nonparallel beam.



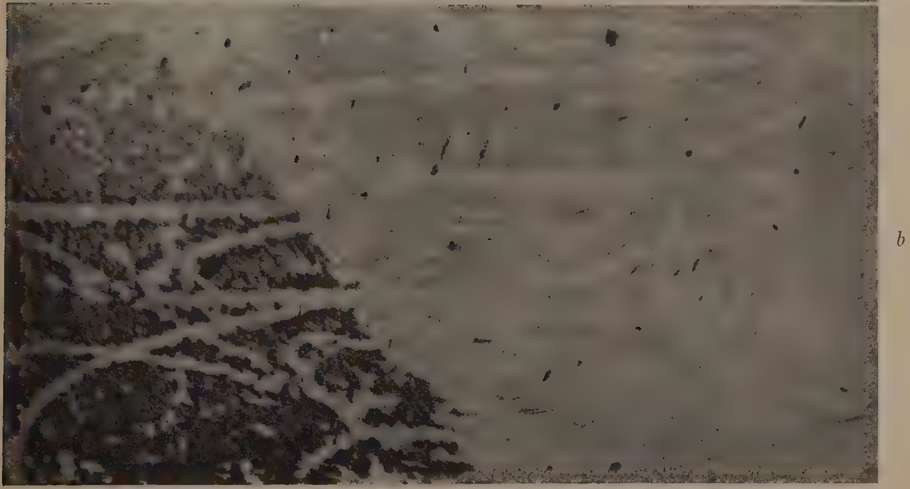


FIG. 14*a*.—POLYCRYSTALLINE LEAD (99.998 PER CENT LEAD) RECRYSTALLIZED, SCRATCHED. × 50. 548-Ortho-thin-coated plate.

FIG. 14*b*.—POLYCRYSTALLINE TUNGSTEN, SCRATCHED. × 50.

This theory predicts that strained areas should fail to give more intense reflections than unstrained areas when: (1) the reflected ray is of low relative intensity, such as the reflections at the large diffraction angles, or (2) when the crystal absorbs both reflecting and nonreflecting rays very quickly, making the penetration of a reflecting ray and a nonreflecting ray about equal, or (3) when the incident beam is highly collimated and provides only substantially parallel rays. Various illustrations in the present series contain weak reflection images in which the strain markings appear with low contrast as compared with the high contrast in the more intense spots, in confirmation of prediction 1 above. Prediction 2 is confirmed by Fig. 14*a*, an X-ray micrograph of polycrystalline lead, and Fig. 14*b*, a crystal of tungsten, both taken with cobalt radiation and therefore fulfilling the condition of high absorption coefficient. Scratches on both appear as white lines, without appreciable blackening of their edges, whereas in the lighter metals, especially aluminum and magnesium, and even in iron, with the same radiation, the images of scratches are either black or have black boundaries. White scratches are accounted for by the rotation of the surface fragments out of reflecting orientation, and white slip lines are sometimes observed for the same reason. Prediction 3 could be tested only by limiting the beam to a divergence of some seconds of arc, which has not yet been attempted.

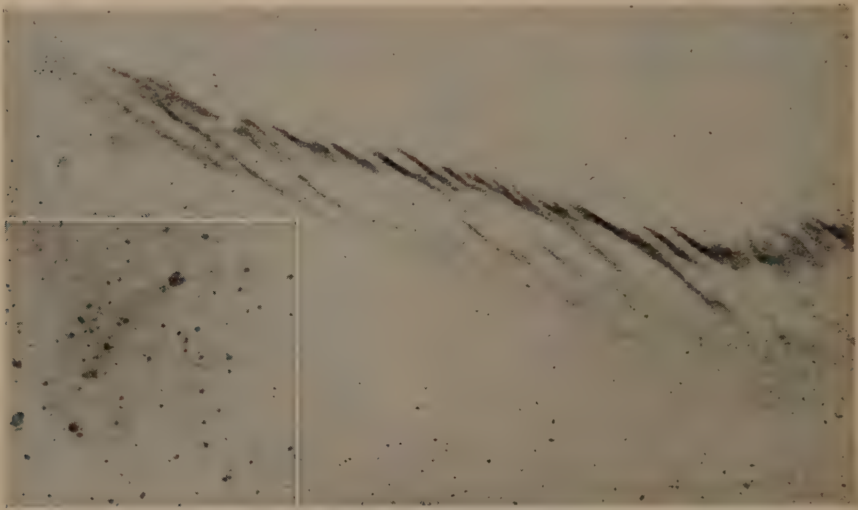


FIG. 15.—LARGE GRAIN OF ALPHA IRON, SLIGHTLY COMPRESSED, ELECTROPOLISHED. × 100 INSERT: PHOTOMICROGRAPH, × 100.

The Nature of Distortion at Slip Lines

Having arrived at a reasonable interpretation of the pictures, let us now explore the possibilities of their use as an instrument for research in physical metallurgy.

It has long been postulated that local rotations of the lattice are to be found near slip lines. I, for one, have often expressed my doubts that the local curvature theory had been adequately proved for metals; certainly the evidence for it in the past has been meager and indirect. But with these X-ray micrographs available there can no longer be any doubt that local distortion does exist along the planes where slip has occurred, and that the distortion resembles the rotation of crystal fragments. In fact, it appears possible to measure the amount by which the lattice at a slip line is rotated (or bent).

The amount of the rotation at an individual slip line has been studied by mounting the deformed crystal in a goniometer and taking a series of X-ray micrographs, with the crystal turned a known amount after each exposure. A crystal of the same silicon ferrite that has been illustrated in the earlier photographs was used; it was deformed slightly in a tensile machine, then mounted in the goniometer. It was found that the crystal could be turned less than 5 minutes of arc beyond the position where the undeformed metal ceased reflecting before the slip lines disappeared in the micrographs. This indicates that the rotation (or bending) at a slip line is several seconds or a few minutes of arc, not the value of many degrees that has been formerly postulated. Probably the displacement at a slip line in this test was too small to produce the maximum rotation, for certainly the deformation given the specimen was mild; on the other hand, perhaps previous experimenters have been misled by more macroscopic rotations of the lattice because of the difficulty of distinguishing them from these microscopic strains at slip lines.

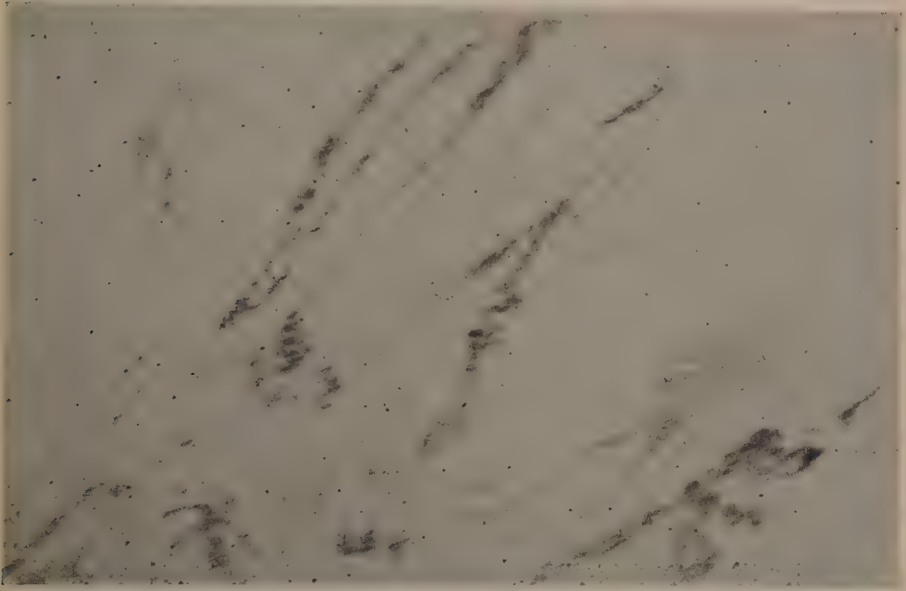


FIG. 16.—LARGE GRAIN OF ALPHA IRON, ELONGATED 3 PER CENT, SECTIONED, ELECTROPOLISHED. × 100.
Highly collimated beam, 548-O-plate.

The striking similarity between the reflecting power along a slip line and along the surface of a scratch, which is evident from Fig. 9 and other micrographs that are not reproduced here, together with the fact that one metallic surface rubs along another in both cases, prompts one to suggest that the conditions of strain at a slip line and at a scratch are quite similar.

A question of fundamental importance to strain-hardening theory is the thickness of the strained region at a slip line. From the widths of the lines in Fig. 10 it appears that the strained region is no more than 3 microns wide on the crystal surface, and since this is about the resolving power of the pictures the true width may be less.

The pictures do not indicate any strain in the regions between these lines, though possibly an improved technique could find some elastic strains here.* Could it be that movement along parallel slip planes would encounter interference from previously active slip planes only when cutting through the material that is dark in these micrographs? If so it would follow that strain-hardening should commence only when the lines become closer than 3 microns. It would then be necessary to propose a different mechanism for any hardening observed before this degree of strain is reached; such a mechanism could be the gradual hardening into inactivity of all regions of abnormally low slip resistance in the crystal, the places where stress concentrations were favorable to slip.

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* I have in mind crystals of high perfection used under conditions of high primary extinction, which were the conditions of my quartz experiment.

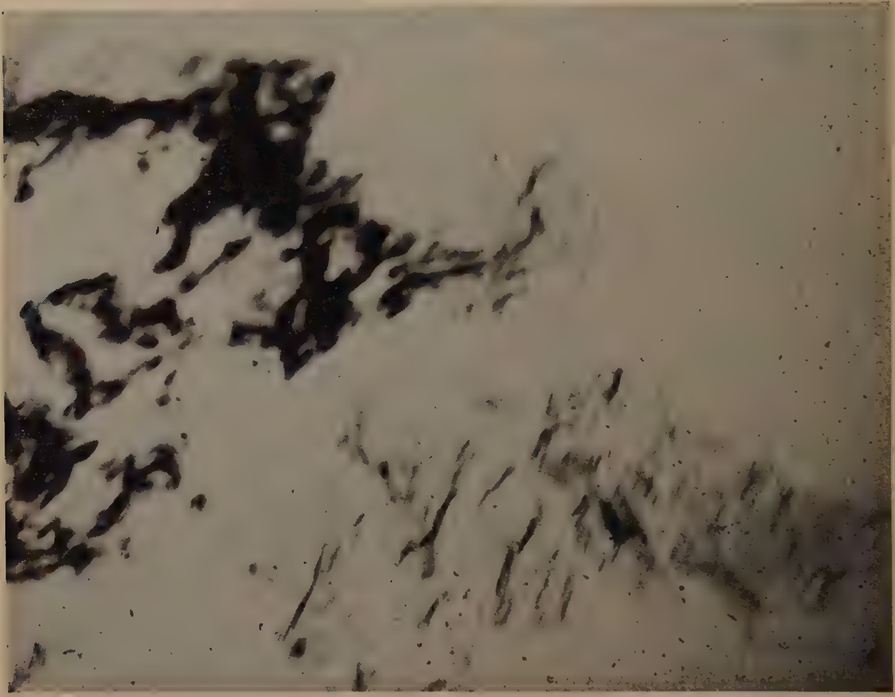

Fig. 17.—Same specimen as Fig. 16. Specimen and plate oscillated 8°. × 50. V-O plate.

It has been proposed by Andrade and others[9] that all strain-hardening could be accounted for by this mechanism of glide starting first at major flaws, later at less grave flaws, and hardening the planes where slip has occurred by the locking action of small fragments of crystal that have been rotated. The present suggestion is that this applies in the early stages of deformation, and that in the later stages slip is forced into the already strained regions.

To carry the speculation further, it would seem reasonable that the strain-hardening of latent slip planes of different orientation should always exceed the hardening of the active set of planes, for the latent planes must cut across the strained regions of the active set.

The importance of obtaining further knowledge of the nature of these distorted regions and their dimensions surely justifies further research along these lines. It seems possible that the electron microscope can provide information of the same kind at much higher magnifications (this is discussed in Appendix II). Further X-ray research might yield quantitative relations between the displacement at a slip line and the degree of the rotation, as well as the width of the distorted band; studies of the intensity of the reflections at these lines might lead to a more complete understanding of the distortion on an atomic scale. Experimenters in this field should be able to obtain a clearer view not only of strain-hardening but also of the process of recovery from strain-hardening, the process of recrystallization, and the strengths and weaknesses of current dislocation theories of plastic deformation.

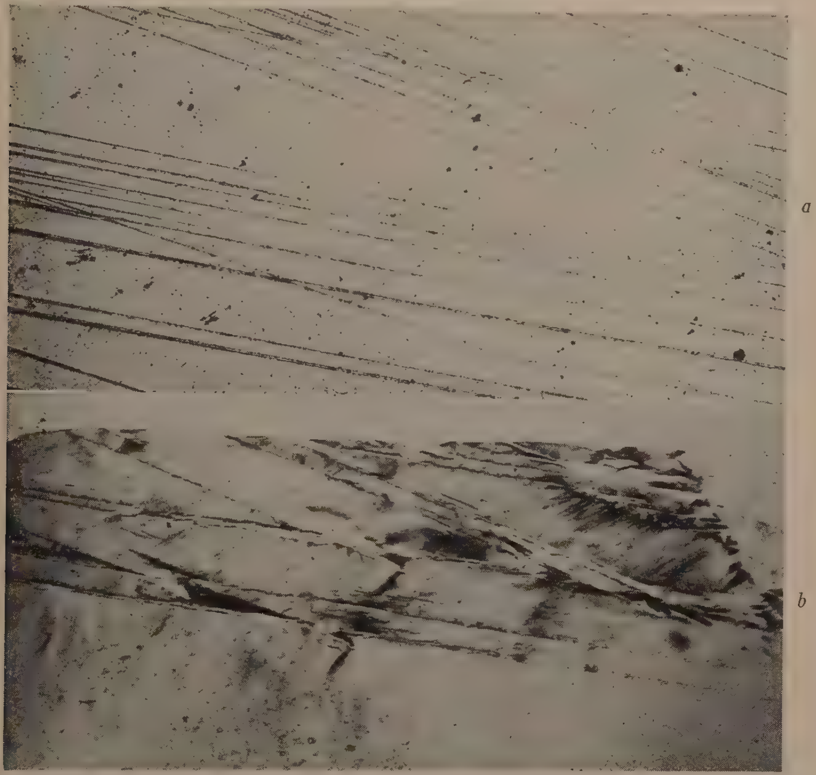

FIG. 18.—SILICON FERRITE CRYSTAL, TWINNED BY TENSION. × 25.
a, optical micrograph; *b*, X-ray micrograph. Top of crystal is 3/16 in. below top of print. V-O plate, 5 min. exposure.

We have seen in the previous pictures that silicon ferrite shows straight slip lines. This is because slip is confined to (110) planes only and it is to be expected that unalloyed ferrite would have wavy slip lines as it does in ordinary micrographs, because of the possibility of slip on many sets of planes. This does occur, as will be seen from Fig. 15, which is a picture of large grains of decarburized mild steel that had been compressed slightly, then electropolished until the surface had the appearance shown in the insert. The X-ray micrograph of this surface shows a featherlike arrangement of wavy slip lines. The main part of the grain reflected too weakly to show in the picture.

Another grain of this iron, a large grain that was in the interior of a ½-in. diameter rod elongated 3 per cent in tension and subsequently brought to the surface by sectioning and polishing, is shown in Fig.

16. In this micrograph a dark line weaves back and forth, composed of fine cross-hatching lines, barely resolved. The pattern results from using a small pinhole at a large distance from the specimen, so that the beam of X-rays from the tube is highly collimated. The interpretation of the pattern is that only narrow bands of material on the crystal are properly oriented to reflect the beam, which in this case contained rays that were parallel within 5 minutes of arc. The band of reflecting material produces a variety of contour map of the wrinkled atomic planes, showing one "level" of orientation as it weaves around on the surface (an isoclinal line). It may be noted that slip lines are seen only in the reflecting bands, and that the lines are very short, indicating again that the disorientation in slip lines is small, a matter of seconds or minutes rather than degrees. The slip-line spacings are 5 microns or less.

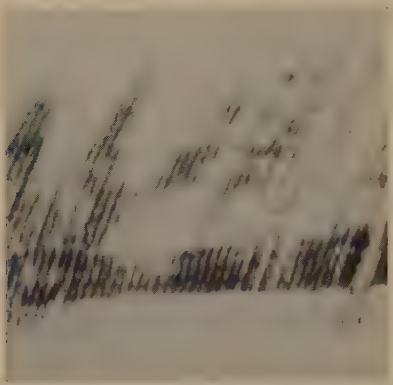

FIG. 19.—DISTORTION FROM LATHE TOOL (VERTICAL MARKS) AND LINEAGE IMPERFECTION (HORIZONTAL BANDS) IN A SINGLE CRYSTAL OF ALUMINUM. × 50.

In another experiment with the same material, the X-ray beam was made effectively very nonparallel, by fastening the specimen to the photographic plate and then oscillating the pair through a considerable angle, using an oscillating crystal camera. Fig. 17 was made in this way with an 8° angle of oscillation. Resolution is not as good as in Fig. 16 because the distance to the plate was greater than before, about 2 mm. A larger proportion of the grains reflect than before, but there are still folds that are tilted out of the range of reflecting angles. All slip lines that can be seen are of the wavy type, characteristic of alpha iron.

Inhomogeneous Distortion from Other Causes

In the 1928 Annual Lecture, Professor Mathewson pointed to the likelihood of inhomogeneous strain at the boundaries of deformation twins. I believe he will be interested to see how his ideas are confirmed by today's pictures. Consider a single crystal of silicon ferrite in which deformation twins have been formed by simple tension. The ordinary micrograph appears as in Fig. 18*a*, and shows numerous twins, the so-called Neumann bands. In an X-ray camera the sample yields a micrograph, Fig. 18*b*, that is full of interesting details that previously were invisible. The magnification here is 100 diameters. Local strain is seen at both boundaries of the twins, for these boundaries are black lines. Furthermore, at the ends of the twins and at some other places, there are concentrations of black lines, indicating a concentration of local slip. A goniometer study of several shows that the rotation at the boundaries of the twins is in the range 0.5° to 1°. This is, therefore, a more severe distortion than occurs at slip lines. (Later figures will show that there is no distortion at the boundaries of annealing twins.) Whole segments of the crystal that lie between certain twins are altered in orientation to a nonreflecting position (the white areas in Fig. 18*b*).

A goniometer analysis was made of the rotation induced by scratching a silicon ferrite crystal with the point of a needle. Clear-cut images of the scratches were obtained and the amount of fragment rotation at the scratches was found to lie between 5 and 10 minutes of arc.

It might be mentioned that by dissolving away successive layers at the surface it would be possible to measure the depth to which disturbed metal extends below the surface; in fact, a succession of goniometer studies could be made at different depths in any cold-worked grain in such a way as to yield a three-dimensional survey of orientations throughout the interior of the grain.

An example of deeply penetrating distortion from a lathe tool is shown in Fig. 19. The specimen was a cylindrical crystal of aluminum, grown from the melt, turned carefully in a lathe, then deeply etched until it was thought that distorted material had been removed, and electropolished. Lathe marks can still be seen running vertically in the picture.

The same figure shows horizontal bands that indicate natural imperfections (lineage structure) resulting from growth. X-ray micrographs would serve well to detect and measure many natural imperfections in crystals, of which the lineage structure in Fig. 19 is only one example. This feature should be of interest to mineralogists, physicists, chemists and may possibly prove important in some commercial applications.

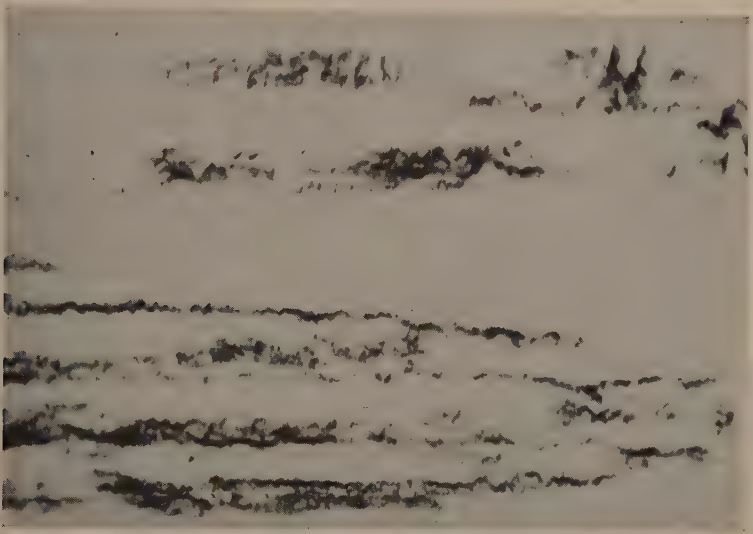

FIG. 20.—DEFORMED ALUMINUM CRYSTAL, SHOWING DEFORMATION BANDS. × 50. V-O plate, 10 min. exposure.

The axis around which rotation from local strains is at a maximum is another interesting feature open to investigation by this type of measurement; in fact, a pole figure could be plotted for the material at the boundaries of a single twin, scratch, tool mark, or perhaps even a single slip line.

The early stages in the formation of deformation bands can be followed by this method, since these bands are readily seen at magnifications below 100 diameters and since they consist of gradually increasing differences in orientation between adjacent regions in the crystal. An example is furnished by Fig. 20, a reflection from a single set of planes in a large crystal of aluminum (99.96 per cent aluminum) in which deformation bands had been formed by a compression of about 7 per cent. Alternate horizontal bands of reflecting and nonreflecting material indicate the nature of the banded distortion. Goniometer studies could give the scatter in orientation at various stages in the deformation and could show the sharpness of the transition region between such deformation bands.

internal strains such as slip lines, with the exception of a few puzzling spots. The graininess that is present in the uniform grayness of the spots is merely the graininess of the V-O plate, since enlargement

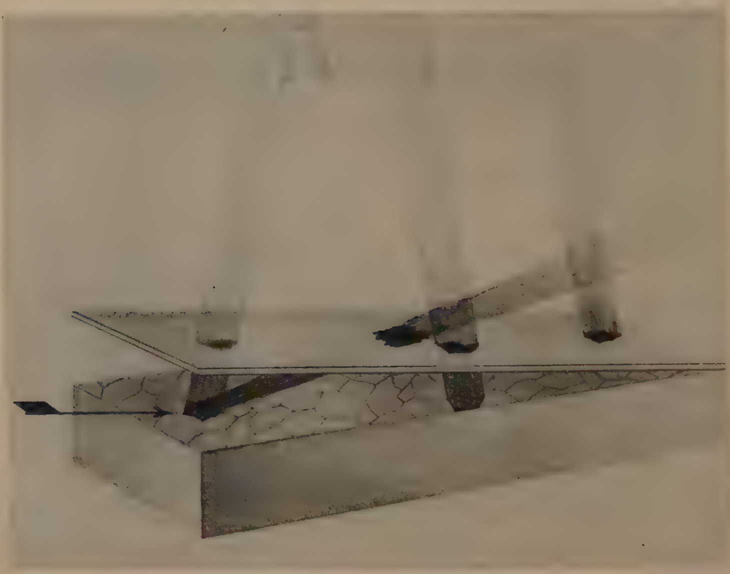

FIG. 21.—ILLUSTRATING REFLECTIONS FROM POLYCRYSTALLINE SPECIMENS. Inclined reflections produce streaked images.

to 50 diameters, as in this figure, is about the maximum for this emulsion. The shapes of individual grains are shown in striking fashion because each reflecting grain is immersed in a group of nonreflecting grains.

Polycrystalline Metals

We turn now to the application of this method to strain-free polycrystalline metals. A block of polycrystalline metal on which rests a photographic plate is sketched in Fig. 21. As indicated in the drawing, only a few of the grains will reflect and the reflected rays will go in various directions. Grains nearest the plate give the best images. Reflected rays that are very oblique to the plate give elongated images. These characteristics are illustrated by Fig. 22, an X-ray micrograph of a strip of commercial purity aluminum (2S-O) after tensile elongation and recrystallization. There are strong and weak reflections, overlapping reflections, and images that are distorted by the angle of incidence of the reflected ray on the plate. Note that the grains are free from

Pictures of polycrystalline materials obviously permit a determination of grain size, perhaps more economically than by other methods in some instances. It may be possible, for example, to dispense with the polishing operation and use the surface of a metallurgical product just as it is received from a hot-rolling or annealing operation, obtaining the results in a few minutes. If many determinations were to be made in routine inspection, it would be found convenient to use a camera on which samples are exposed to a roll film, with a mechanism provided for bringing successive "frames" of the film into position.

Fig. 23 illustrates the relation of the conventional to the new micrographs for normalized mild steel. Both prints are at the same magnification. When the photographic plate is approximately parallel to the specimen surface, grain size is indicated by the diameter of equiaxed spots, and might be determined by comparing the spots with the customary standards in a chart or a grain-size eyepiece. The width of the elongated spots is also a true measure of grain size, because the elongation is merely the result of an oblique incidence of the rays on the photographic plate, which leaves the width unaltered and increases only the length of the spots. (The major axis of an elongated spot, incidentally, points toward the grain that caused the spot.) By counting the spots, it is clear that about one grain in ten caused a spot

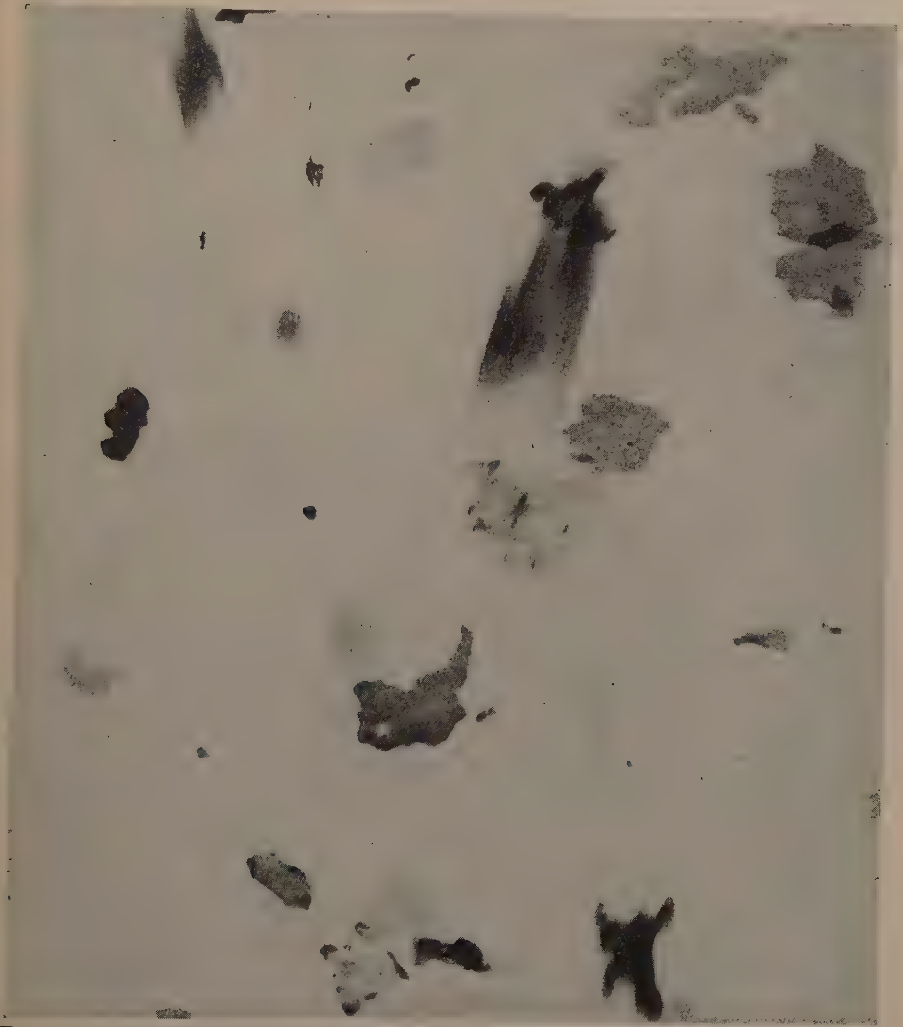

FIG. 22.—COMMERCIAL ALUMINUM STRIP (2S-O), RECRYSTALLIZED, ELECTROPOLISHED. × 50. V-O plate.

in the X-ray picture; this ratio would, of course, depend upon the exact focal spot dimensions and the distances in the X-ray camera.

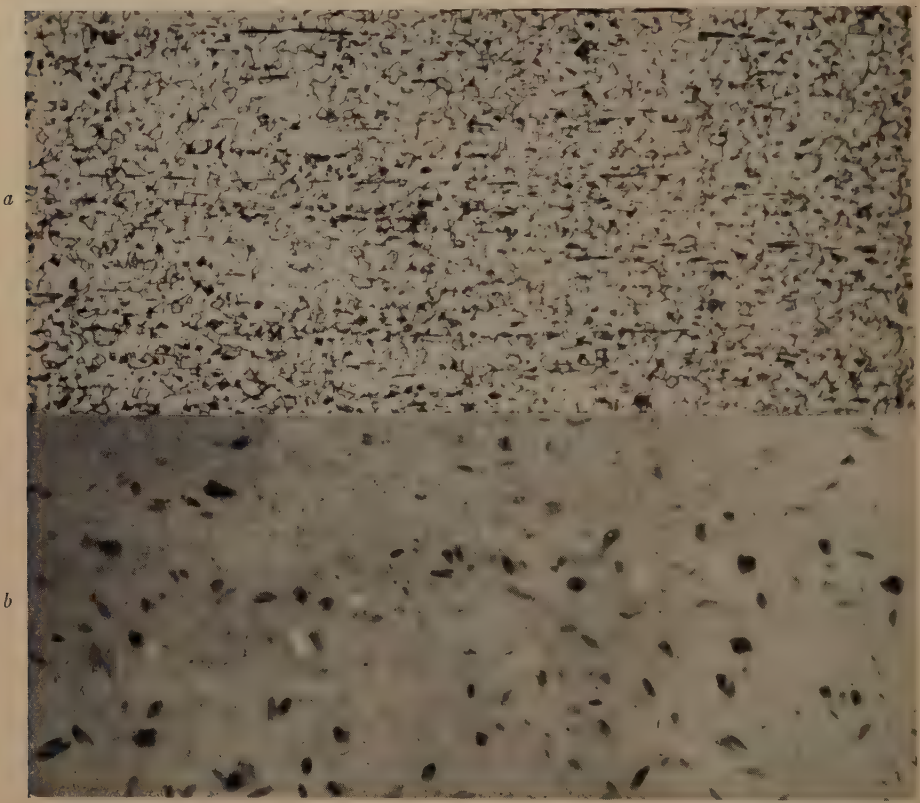

FIG. 23.—NORMALIZED MILD STEEL, × 100.
Optical photomicrograph above, X-ray below at same magnification. 548-O plate.

Microstructures of familiar appearance are obtained with brass (Fig. 24). This specimen is of annealed cartridge brass deeply etched to a somewhat wavy surface that produces a rippled appearance in the X-ray images. Annealing twins are very prominent, and there is no concentration of strain at the boundaries of the twins. Some of the long narrow streaks are reflections from twins of grains that did not otherwise reflect. This illustration was prepared with an oscillating specimen-and-plate camera, which provided a greater number of reflections than the stationary type. Another example of the registration of surface contour is reproduced in Fig. 25. A recrystallized grain in a sheet of silicon ferrite is shown here after deep etching with nitric acid. Each etch pit casts shadows in the very oblique "light" from the X-ray tube so that only the projecting ridges reflect to form the black marks in the picture.

Among the miscellaneous possible applications of this method to polycrystalline metals should be listed the study of subgrain boundaries, alpha veining in iron, "suture lines" and the like, for a photograph or a series of exposures on a goniometer could distinguish a perfect grain from a

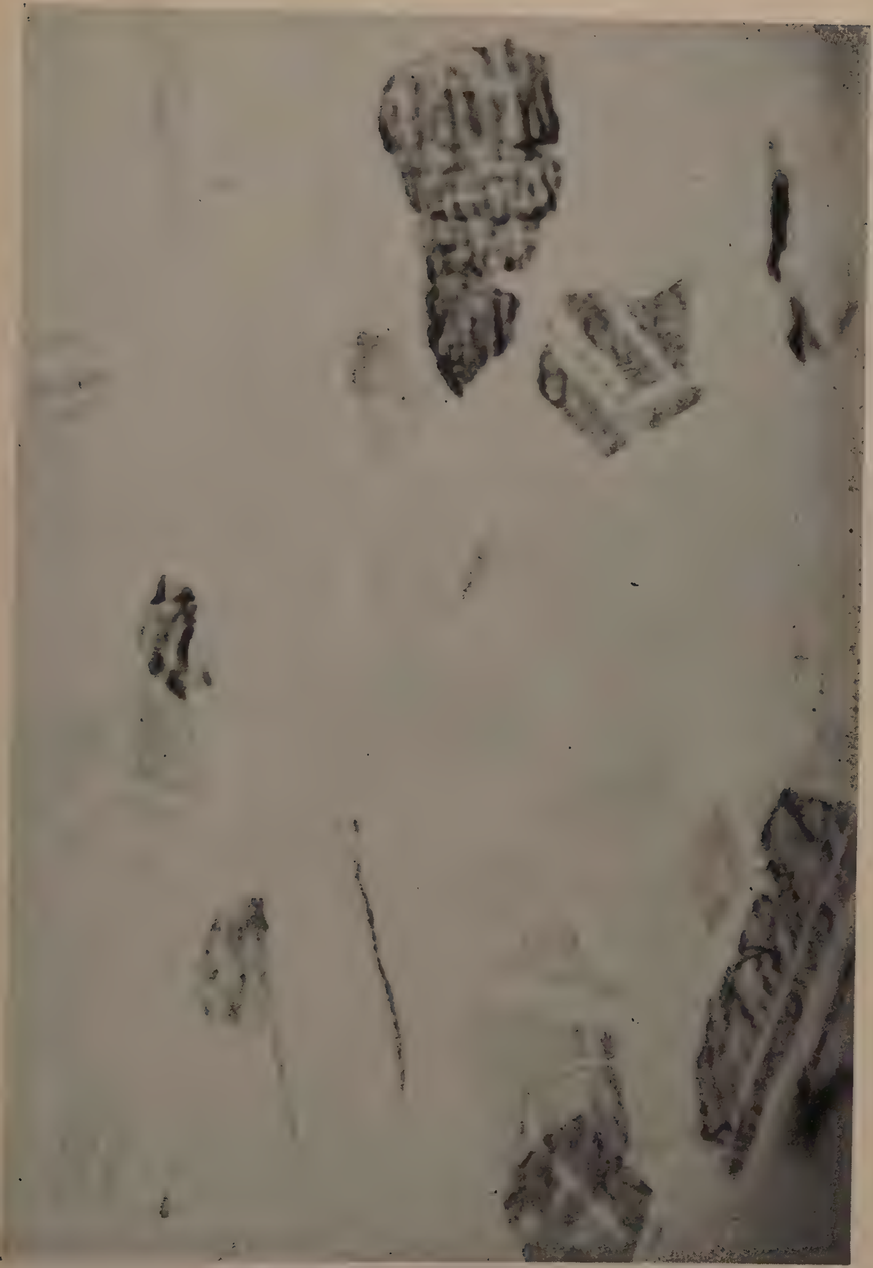

FIG. 24.—CARTRIDGE BRASS, RECRYSTALLIZED, ETCHED TO RIPPLED SURFACE. × 50. Specimen and plate oscillated 10°. V-O plate.

preferred orientation of subgrains having a divergence in orientation of minutes of arc or more. The method serves to distinguish recrystallized grains from cold-worked grains (even when they are the same size and shape), annealing twins from deformation twins, and crystalline particles from amorphous particles. In some fields it might prove of value in distinguishing single-crystal particles from particles that are aggregates. It may have uses in showing the internal structure of minerals and precious stones.

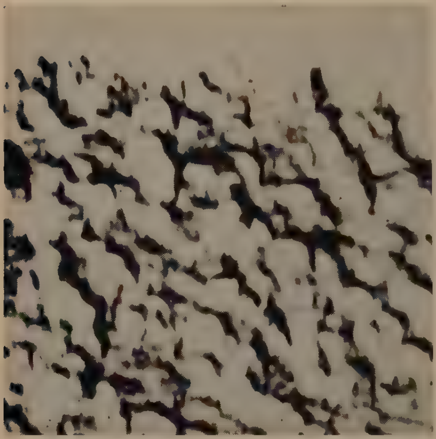

FIG. 25.—RECRYSTALLIZED GRAIN OF SILICON FERRITE, SHOWING ETCH PITS. × 50.

Deformation from the Tensile Test

A great many studies of the deformation of grains by applied loads have been made with X-rays; one result of plastic flow is to produce "asterism" in Laue photographs, a lengthening of Laue spots into streaks that results from a spreading range of orientation in each grain. This feature has been extensively studied by Prof. G. L. Clark and others. Pictures of the orientation divergence in individual grains have also been prepared with a camera in which the specimen and film oscillate together in a beam of monochromatic radiation.[10]

It has been established from these earlier studies that a complex spreading of lattice orientation takes place in each grain as deformation proceeds, with rotation occurring about several axes by amounts that increase with increasing deformation. The present technique makes it possible to see the microscopic features of this process, which may aid us as we grope for an understanding of the strengths of metals and of strain-hardening. In earlier sections, for example, we have shown that deformation bands and irregular lattice buckling are responsible for the large ranges of orientation that cause asterism, whereas the narrow distorted bands at slip lines appear to be minor contributors.

The illustrations to follow are on tensile tests of aluminum. When the sample of aluminum shown in Fig. 22 is elongated 1 per cent in tension there is no visible elongation of the grains, of course, but an X-ray micrograph (Fig. 26) shows that the internal structure of the grains is much distorted. Grains are crossed by lines and bands, and some are distorted so that only irregular patches reflect. In some grains only the areas around the grain boundaries reflect. When the elongation is increased to 20 per cent the distortion of the grains is severe and the resulting pattern is intricate (Fig. 27). Individual grains can still be recognized by the clustering of the dots or dashes that come from them, but large sections of each grain are warped out of reflecting position. The sizes of the dots and the widths of the dashes suggest that the grains are now reduced to units that are remarkably uniform in size, of the order of 5 microns on a side (0.005 mm.). A term often used by H. J. Gough, W. A. Wood and other English metallurgists seems quite appropriate for these units: "Crystal fragments."

It appears likely that the dots in these images are the direct result of multiple sets of finely spaced slip lines. Perhaps they are the points where slip lines cross each other and produce more severe rotations than elsewhere, or perhaps they are reflections from distorted boundary material around more perfect mosaic fragments, or, again, they may be the images of the fragments themselves slightly disoriented from each other. Whatever may be learned ultimately concerning their fine-scale interpretation, it seems safe at this time to assume that they give us a view of the distribution of peak values of the microstrains in a grain, and that they show the points of high microstress in cold-worked material.

We may summarize by saying that the micrograph provides, in effect, a map of the strain peaks over a surface that may be either external or internal at the time of deformation.

If this interpretation is correct, the structure of cold-worked metals that is revealed by this method is of considerable importance to metallurgists, physicists and chemists. The points of high microstrain, we must assume, are points where the strain energy is concentrated in large measure, points where resistance to slip is high, and where the resistance to the flow of electric current is high; points where the rate of nucleation and the rate of growth of recrystallized grains must be high; points where the nucleation for a phase transformation is high and where the transformation front moves most rapidly; points where chemical reactions should proceed most rapidly and possibly, also, points where stress-corrosion cracking or season cracking may begin.

From the large number of dots in the image of a single grain we conclude that there are fragments numbering in the hundreds on a single cross section through a grain. Before the total number of fragments could be determined, the exact depth below the surface that is contributing to the picture would have to be carefully considered; in these particular grains the number of fragments must lie in the thousands. Further investigation may show that the

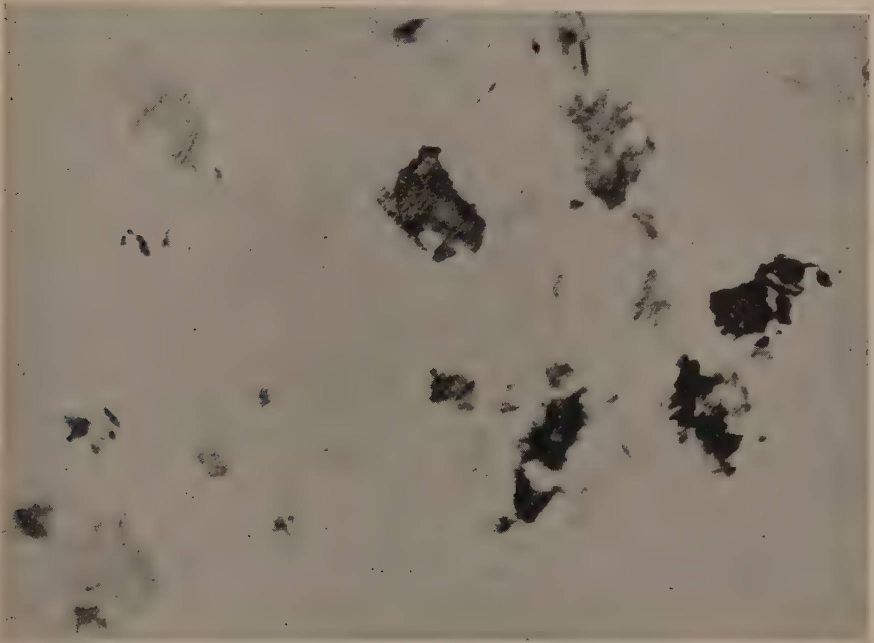

FIG. 26.—COMMERCIAL ALUMINUM (2S-O) ELONGATED 1 PER CENT, ELECTROPOLISHED. × 50.

number of dots and their size correlate in some way with rates of recrystallization, or the degree of strain-hardening, or the amount by which other physical properties are altered by cold-work.

There is another factor that should be mentioned, in addition to the number of microstrain peaks, that may influence the properties of cold-worked metals and that may be studied by pictures such as these—this is the factor of preferred orientation of the fragments. The difference in orientation between adjacent fragments may be judged to be particularly important in causing increased resistance to slip, for Chalmers has found such an effect in tensile tests of large bi-crystals.[11]

It is possible to obtain detailed information on the scatter of orientation in a cluster of fragments by placing a photographic

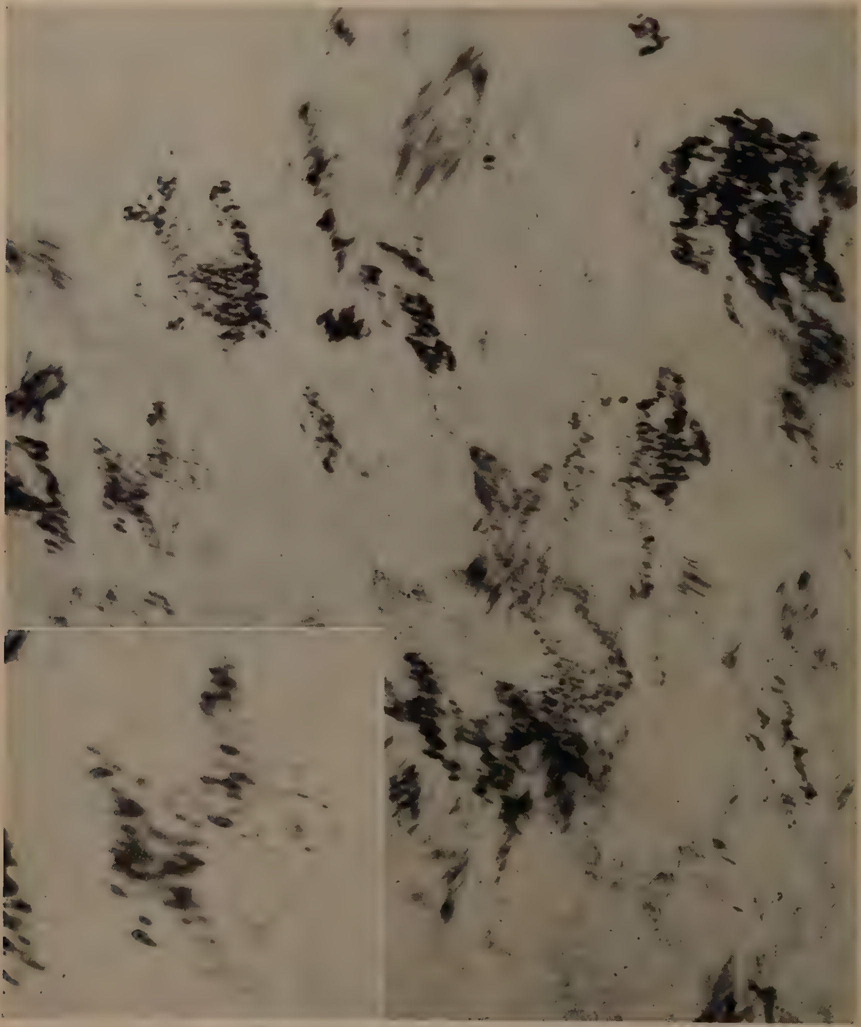

FIG. 27.—SAME ALUMINUM AS FIGS. 22 AND 26, ELONGATED 20 PER CENT, ELECTROPOLISHED. × 50. INSERT IS × 100.
548-O plate.

plate at a somewhat greater distance from the sample and comparing the image on that negative with the image of the same grain on a plate in contact with the sample. Or the reflected rays may be made to pass right through the nearest film and make a record simultaneously on a second emulsion at a distance, thus providing two negatives with comparable images. An analysis of the two images then gives the orientation of the reflecting plane.

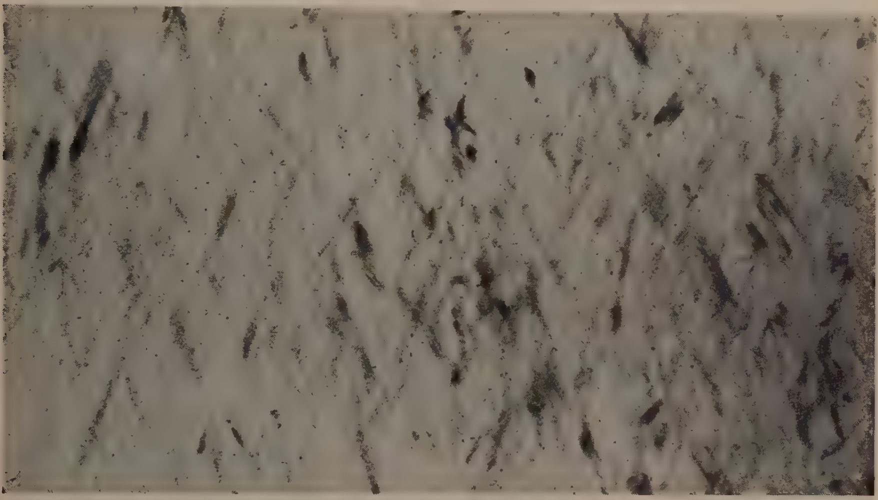

FIG. 28.—LOW-ALLOY FERRITE (0.83 PER CENT CR), ELONGATED 35 PER CENT, SECTIONED, ELECTROPOLISHED. × 50.
Incident beam went from left to right.

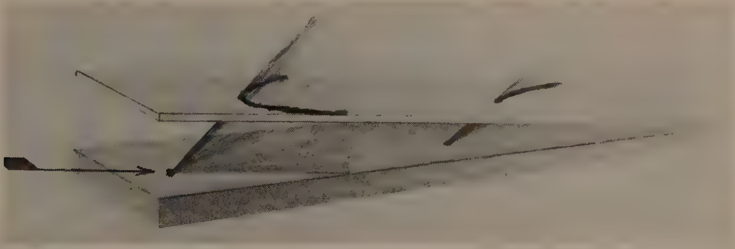

FIG. 29.—CONES OF DIFFRACTED RAYS FROM GRAINS IN A COLD-WORKED SPECIMEN (BELOW) INTERSECTING A PHOTOGRAPHIC PLATE (ABOVE).

A tensile specimen of a ferritic alloy (0.83 per cent Cr in Fe) gave the pattern of Fig. 28. The specimen had an A.S.T.M. grain size of 3 to 4* and was in the recrystallized condition prior to testing. The broken specimen was sectioned longitudinally and carefully ground, deeply etched, and repeatedly electropolished. The area shown in this figure had been elongated about 35 per cent (effective deformation 0.30). At this deformation, according to the stress-strain curve, strain-hardening had carried the true stress up to 45,100 lb. per sq. in., where the linear portion of the true-stress vs. effective-deformation curve begins.

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* The specimen was the fifth entry in Table 1 of a paper by C. E. Lacy and M. Gensamer.[12] The 0.2 per cent offset yield strength was 6000 lb. per sq. in.; tensile strength, 33,550 lb. per sq. in.; reduction of area, 91 per cent; elongation, 60 per cent in 1 inch.

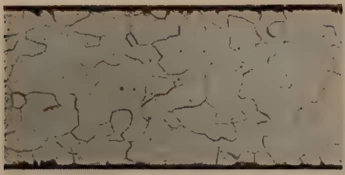

FIG. 30.—OPTICAL PHOTOMICROGRAPH OF CROSS SECTION OF SHEET ALUMINUM USED FOR FIG. 31. × 50.

Analysis: 0.004 per cent Si, 0.004 per cent Fe, 0.006 per cent Cu, 0.001 per cent Ti, balance Al; 345 grains per square millimeter.

Prominent features of this micrograph are the long streaks made by the highly distorted metal in individual grains, signifying a considerable spread of orientation in each grain. An understanding of the streaks may be had from the sketch in Fig. 29.

If the incoming beam is indicated by the arrow at the left, a single grain in the block of metal will send out reflected rays along some of the generators of a cone, the cone being concentric with the incoming beam. (This cone is the one that forms a ring on a powder diffraction photograph, not the one pictured in Fig. 4.) The cone intersects the photographic plate in a hyperbola, as indicated in the upper part of the sketch. The apex angle of the cone will be 4θ, where θ is the angle of incidence on the particular set of atomic planes that is reflecting the rays. If the range of orientation is large, a large segment of the cone will be registered on the plate, but in general only a small portion of it will be found (for those crystal positions where Bragg's law is fulfilled), like the partial cone sketched at the right of this figure. The nearer the reflecting grains are to the plate, the longer these segments of parabolas are, and the more nearly they will indicate the apex angle of the cone, a fact we shall refer to in another connection later.

A series of tensile experiments on high-purity aluminum of two different grain sizes is illustrated in Figs. 30, 31, 32 and 33. These figures present photomicrographs of the cross section of each lot of the aluminum strip, and show the changes in the X-ray micrographs that result from varying amounts of deformation. It is evident that grain fragmentation is very slight after an elongation of 1.0 per cent in both samples, and severe after elongations of 5.0 per cent or more in both. In both, likewise, the fragments are about the same size. Judging by the widths of the minute dashes, they are all approximately 5 microns across, just as in the high-purity aluminum of Fig. 27.

Gradually increasing deformation in every case seems to make the dots more clearly seen as individual black spots separated by white, rather than to reduce their size. It is as if each dot represented a fragment that was becoming increasingly different in orientation from its neighbors, sending its reflected beam in a direction increasingly different from neighboring fragment reflections. At an elongation of 5 per cent the dots have scarcely separated enough to be resolved and they form curious irregular patterns within the area of the original grain, marking out what we have described as isoclinal lines. At 20 per cent elongation they have spread so that it becomes difficult to recognize the clusters that belong to any individual grain.

Regarding Recrystallization and Recovery

It is curious that a study of Figs. 31 and 33 does not immediately disclose a feature that would account for the great difference in the rate of recrystallization in the two samples when given the same amount of deformation. In a study of this material by R. F. Mehl and W. A. Anderson,[13] it was found that the rate of growth of recrystallized grains in the material with smaller grain size was 6.5 times as great as in the other during annealing at 350°C.

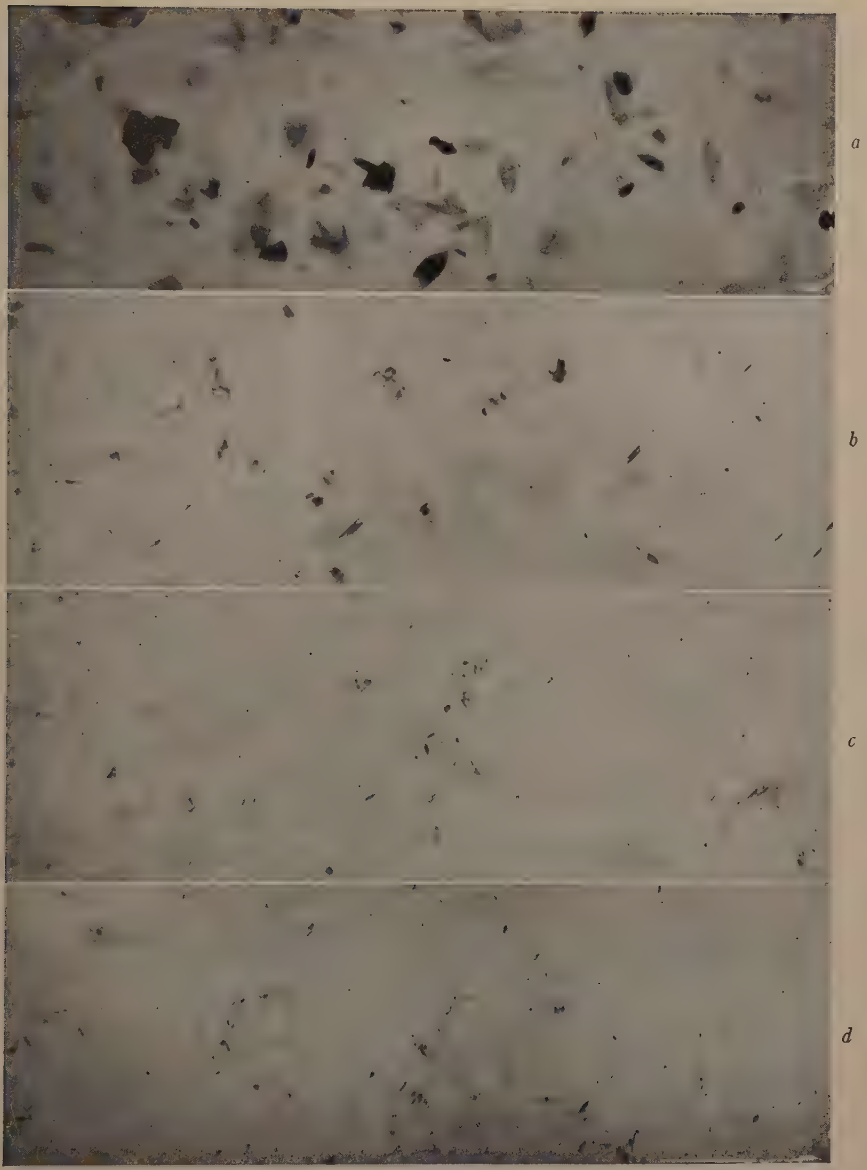

Fig. 31.—Aluminum of Fig. 30 after tensile elongation. Electropolished. × 50. Elongations as follows: *a*, 1 per cent; *b*, 5 per cent; *c*, 10 per cent; *d*, 20 per cent.

after a 5 per cent elongation in tension. To understand this difference one should consider the following structural features of the cold-worked grains: (1) the distribution of strain from the edge to the center of the average grain, (2) the number of points of high strain, (3) the intensity of the strain at these points, (4) the orientation relationships among neighboring fragments, and (5) the size or size distribution of the fragments. Some of these characteristics, perhaps most, are within the reach of the techniques presented in this lecture but the answers to questions of recrystallization rates are not obvious from the small amount of experimental work I have done on the subject.

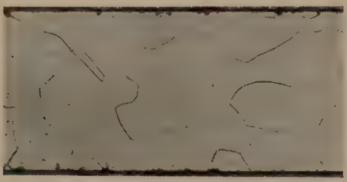

FIG. 32.—PHOTOMICROGRAPH OF ALUMINUM USED FOR FIG. 33. × 50.

Analysis as for Fig. 30, 60 grains per square millimeter.

Fig. 34 represents a sample of large-grained, high-purity aluminum, (the material of Figs. 31 and 33) elongated 5 per cent and subsequently annealed until 98 per cent of the material was recrystallized. The picture, taken at one of the least recrystallized areas on the specimen, shows some of the few remaining unrecrystallized grains and one of the smaller recrystallized grains (at the lower right).

The striking difference between images of recrystallized and unrecrystallized grains should make X-ray micrographs of value in recrystallization research. The recrystallized grain so easily seen in Fig. 34 could hardly have been distinguished from its cold-worked neighbors in an ordinary micrograph, for it resembles them in size and shape. Therefore, early stages in the growth of recrystallization nuclei can be followed by these diffraction pictures with much more certainty than formerly. It should be possible to determine the rate of growth of an individual grain by returning a specimen to an identical position in a camera after each of a series of annealing treatments. If the grain grows at different rates in different portions of its perimeter, this too should be measurable.

Obviously the specimen of Fig. 34 has been given about as much annealing as it is possible to give this material in the cold-worked state, yet apparently there is no change in the structure of the cold-worked grains. No change other than stress relief in the fragments is likely, a straightening of atomic planes in each fragment, and perhaps some may question whether even this has occurred.

The values of the rates of nucleation and growth for recrystallization are left unchanged by recovery in the material of this aluminum, as Dr. Mehl and Mr. Anderson have shown, so it might be argued that prior to recrystallization the alterations in the cold-worked structure could be only minor ones. There is a slight but positive effect of recovery on recrystallization rates in iron-silicon alloy containing 1 per cent silicon, as J. K. Stanley* has shown in a current paper, but a study of his samples again disclosed no alteration of structure in the strained grains, even when annealing was prolonged until recrystallization was 95 per cent complete. Fig. 35*a* was taken after a slight anneal that caused no recrystallization, and Fig. 35*b* represents one of the least recrystallized areas of the sample that was 95 per cent recrystallized.

These results lead one to predict that the power to recrystallize will remain as long as the grains retain this characteristic fragmented structure. Since no case is known where recovery entirely removes the capacity of a metal to recrystallize, we predict that no recovery treatment will remove the fragmented character of the images in X-ray micrographs, regardless of the effect of recovery on the widths of X-ray diffraction lines.

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* The material of this experiment[14] contained 1 per cent silicon, had an A.S.T.M. grain size of 6.0 and was cold-worked 7 per cent prior to the 35-min. annealing at 770°C.

Inhomogeneous Strains in Cast Metals

Recrystallized grains can be made quite free of strains, as illustrated by the preceding micrographs, but the mechanism of freezing is known to be productive of imperfections in the crystal lattice, segregations, plastic flow, and internal stresses. Cast metals, then, should be an attractive field for investigation with the present method.

Grains of cast aluminum are shown in Fig. 36. The specimen was a small melt of 99.9+ per cent aluminum, poured from a crucible on a firebrick and allowed to cool in air. Fig. 36*a* is a reflection from the outer surface after electropolishing, near an area where dendrites could be seen on the surface. Fig. 36*b* was made on the cross section of the ¼-in. thick slab, after careful preparation and deep electropolishing. Freezing has produced highly imperfect grains. Microstrain peaks occur at intervals of the order of 0.02 mm. in some grains

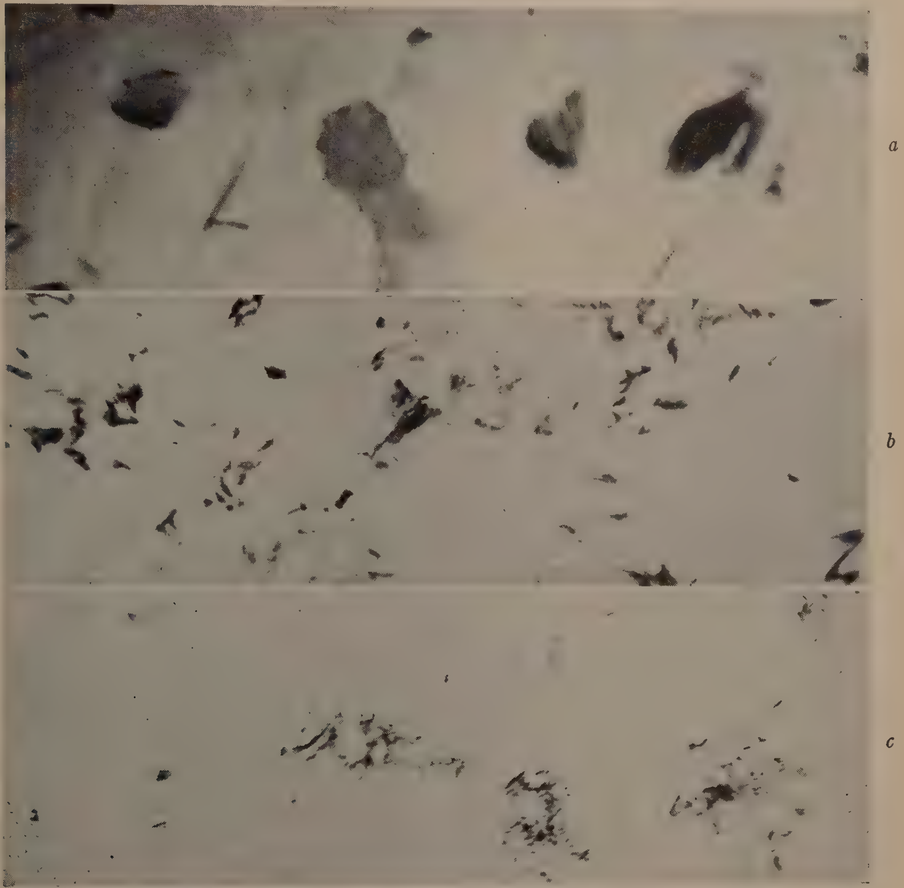

FIG. 33.—ALUMINUM OF FIG. 32 AFTER TENSILE ELONGATION. ELECTROPOLISHED. × 50. Elongations as follows: *a*, 1 per cent; *b*, 5 per cent; *c*, 10 per cent.

and a honeycomb structure is visible in others. (Perhaps these will prove to be different aspects of the same structural imperfections.)

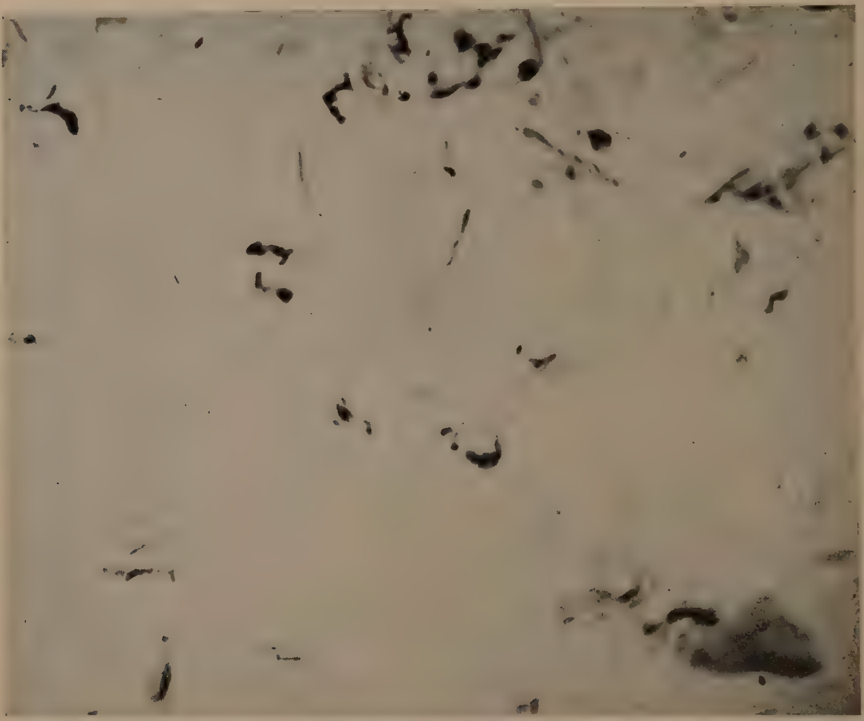

FIG. 34.—PARTIALLY RECRYSTALLIZED ALUMINUM. × 50.
Specimen of Fig. 32, annealed 84½ hours at 350°C. Electropolished. Recrystallized grain at lower right.

Cast high-purity magnesium yields striking pictures (Fig. 37) with periodic black lines of strain and numerous twins (white bands). The grains of Figs. 37*a* and 37*b* are on a cross section of an ingot that was cast in a 2 by 2 by 10-in. mold.

Extreme imperfection must be the rule when dendritic segregation (coring) is present in alloys. This is indeed the case, if we are to judge by Fig. 38 of the cast brass (70 per cent Cu, 30 per cent Zn). The optical and X-ray pictures of the same polished and etched surface are at the same magnification (50X), though they are not necessarily of exactly the same area. In the X-ray micrograph (Fig. 38*b*) the intricate tracery within each reflecting grain marks out the dendritic arms that are seen within the grains of the optical micrograph (Fig. 38*a*). Reflection has occurred only along certain contour lines of favorable lattice orientation on the dendrites.

In cored alloys there is an additional factor that should be considered in interpreting the pictures: the varying lattice constant that results from the varying composition. With most alloys this would have a minor effect on the patterns, but in some the Bragg angle for reflection could be shifted enough to prevent reflection from some areas on a grain.

This example of coring thus opens up a field for interesting study, for it appears readily possible to study the variations of orientation within a single grain and even within a single dendrite area, and possibly also the variation of lattice constant in the same areas. It may be possible to show coring in this way in alloys where metallographic etching fails to bring out the segregation suitably.

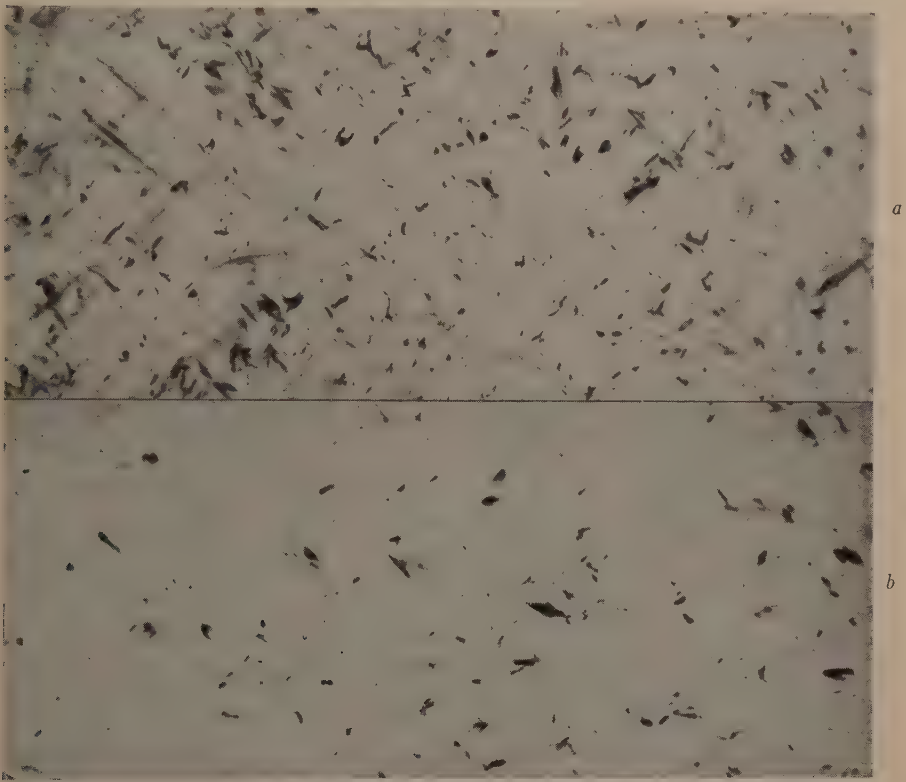

Fig. 35.—Silicon ferrite (1 per cent silicon) A.S.T.M. grain size 6.0. Electropolished. × 50.
a. Annealed 5 minutes at 770°C.
b. Annealed 35 minutes at 770°C.

Polyphase Alloys

The lamellar structure of coarse pearlite is barely within the present resolving power of the method, as is seen from Fig. 39. The specimen was a steel analyzing 0.70 per cent C, reacted isothermally at 700°C. The dimensions of the pearlite colony (see photomicrograph Fig. 39*a*) are similar to the dimensions of the clusters of dashes in the X-ray picture, suggesting that at least some nodules contain lamellae that possess a single crystallographic orientation throughout the colony, for which there is evidence from other investigations.[15] The elongated nature of the spots is a result of the small angle at which the reflected rays struck the photographic plate.

The structures of eutectics resemble rather closely the structure of pearlite when examined by this method as shown in Fig. 40, in which optical and X-ray micrographs are reproduced for an alloy of indium and tin (50.79 per cent Sn) of approximately the eutectic composition. Prominent clusters of X-ray spots here again indicate groups of similarly oriented crystals. Since these spots are disconnected and do not form a continuous network, it is presumed that they come from the white constituent in the optical micrograph, which is the tin-rich phase, rather than from the black indium-rich phase, but no detailed analysis has yet been made of this. More positive identification of the spots in Figs. 39 and 40 could be obtained by the methods that will now be discussed.

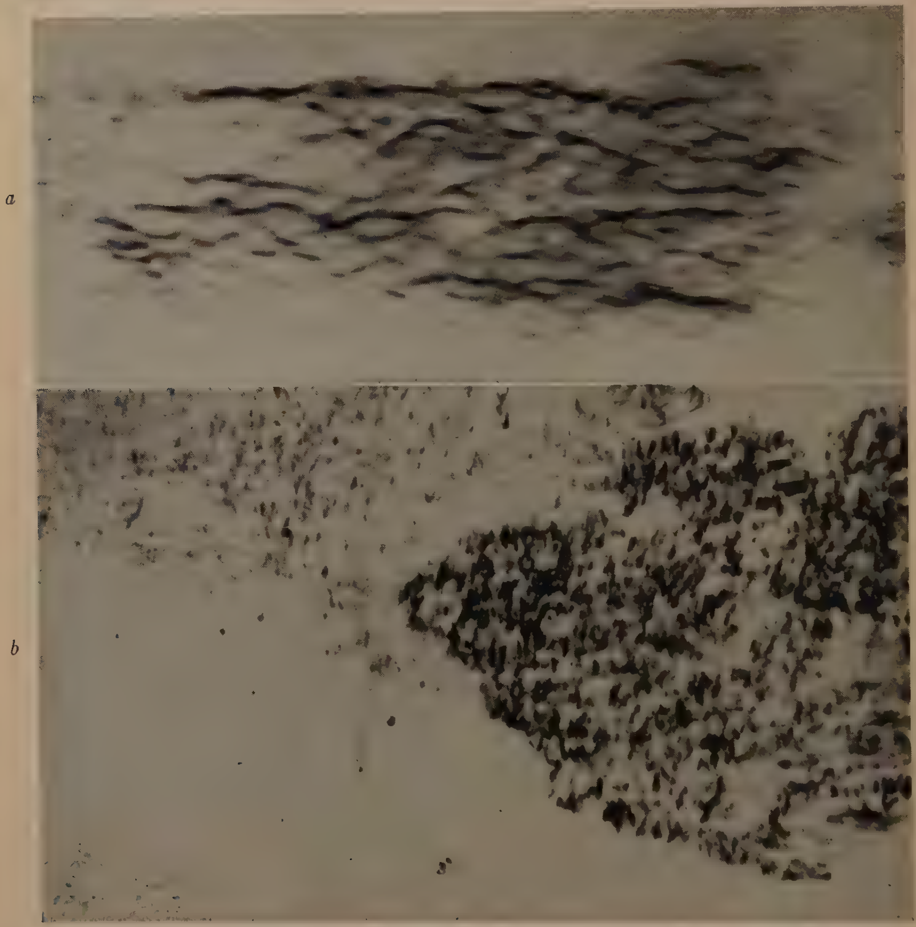

FIG. 36.—CAST ALUMINUM (99.9 + PER CENT ALUMINUM). ELECTROPOLISHED. × 50.
a. A grain at the surface.
b. Grains on a cross section.

Identification of Microconstituents

Properly prepared X-ray micrographs provide a means of identifying constituents of microscopic size in heterogeneous samples, thus a method for microscopic chemical analysis. The basis for this lies in the fact that the angle between each reflected ray and the incident beam is characteristic of the crystal structure of the reflecting crystal, since it is governed by the spacing between planes of atoms in the crystal. It is possible to measure the direction of the reflected ray by having the ray strike two photographic plates at different distances from the specimen. The same ray is recorded on each emulsion and the relative displacement of the spots appearing on the pair of emulsions discloses the direction of the ray in space. If films are used, the two photographs can be made simultaneously, for the reflected ray will penetrate the first film and record itself on the second one, behind the first. In fact, the device can be still further simplified by employing a double emulsion film with emulsions coated on both sides of a thick cellulose base.

An example of a double emulsion picture of a twinned grain of alpha brass is given in Fig. 41; the negative in this case was X-ray dental film. To determine the angle between incident and reflected rays, which is twice the angle θ of Bragg's law, an enlargement may be made with a long-focus lens, so that both emulsions are in focus, then the distance between corresponding points of the two images can be measured. The apparent direction of the displacement is also determined, as well as the spacing of the emulsions. The measurements may also be made directly on the original negative by using a microscope equipped with a graduated rotating stage.

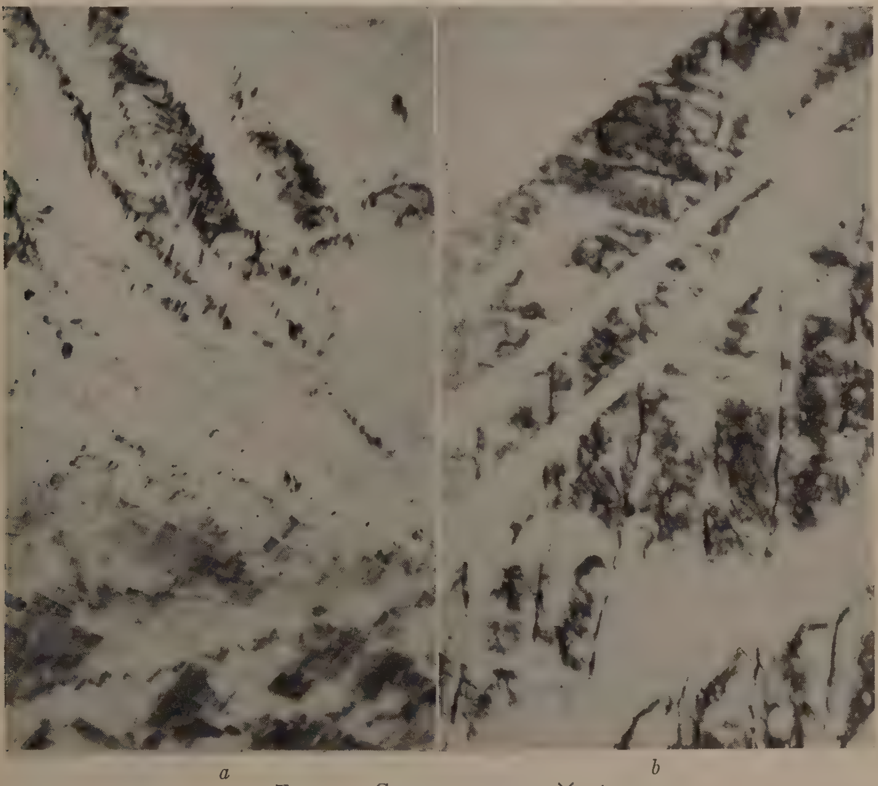

FIG. 37.—CAST MAGNESIUM. × 25.
Melted from distilled crystals; ingot sectioned, mechanically polished and etched repeatedly.

Referring to Fig. 42, let the incident ray be parallel to the photographic film and be indicated by the arrow *OQ*, the reflected ray by *OP* and the separation of the emulsions by *t*. Then, when viewed from a point directly above, along the line *OS*, one image will appear to be displaced a distance *c* from the other and the apparent angle between this displacement and the initial

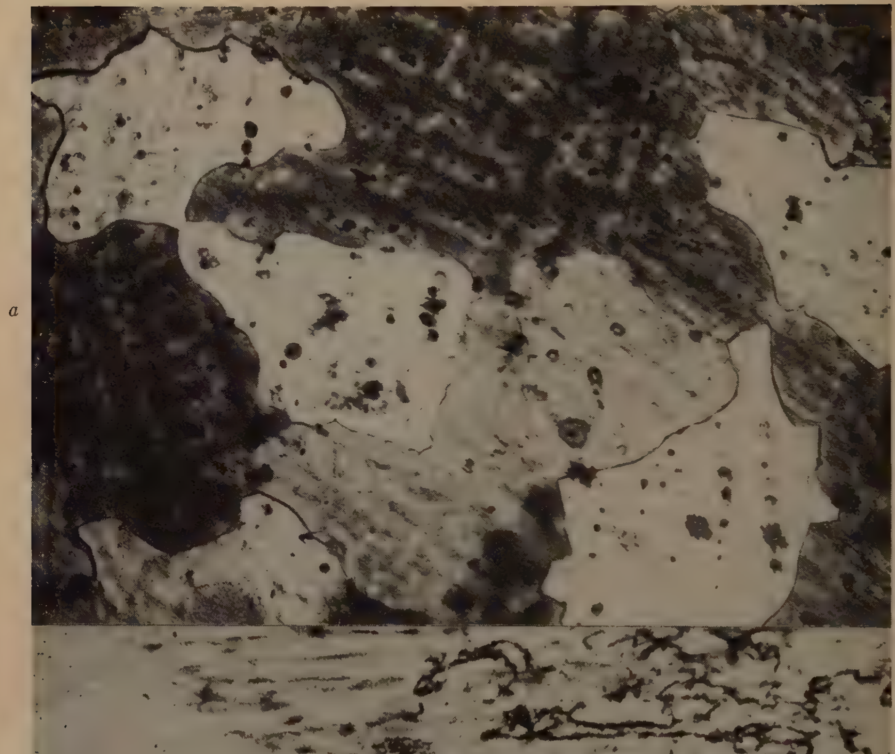

FIG. 38.—BRASS (70 PER CENT COPPER, 30 PER CENT ZINC) AS CAST. × 50.
Mechanically polished and etched repeatedly.
a. Optical photomicrograph.
b. X-ray micrograph of a different area.

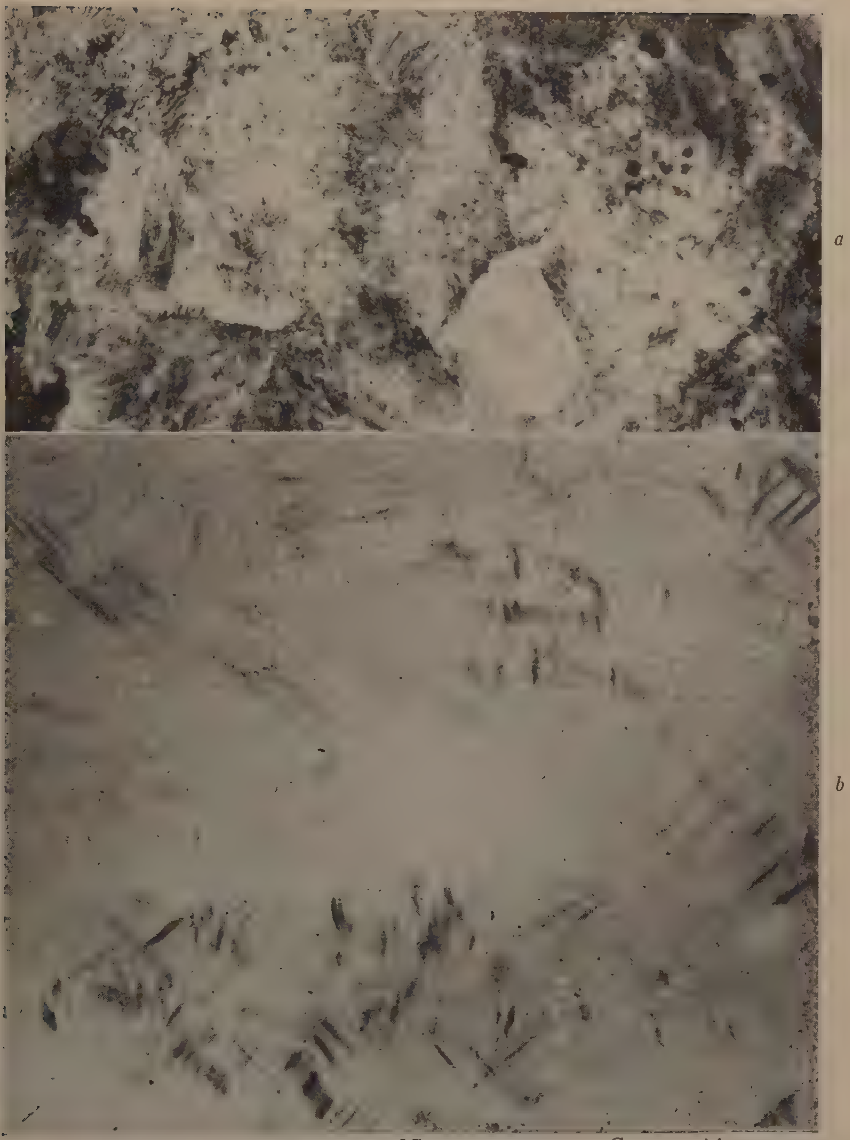

Fig. 39.—Pearlite, formed at 700°C. in 0.70 per cent C steel. × 250.
Mechanically polished, etched 3 per cent picral.
a. Photomicrograph.
b. X-ray micrograph of a different area of the same specimen.

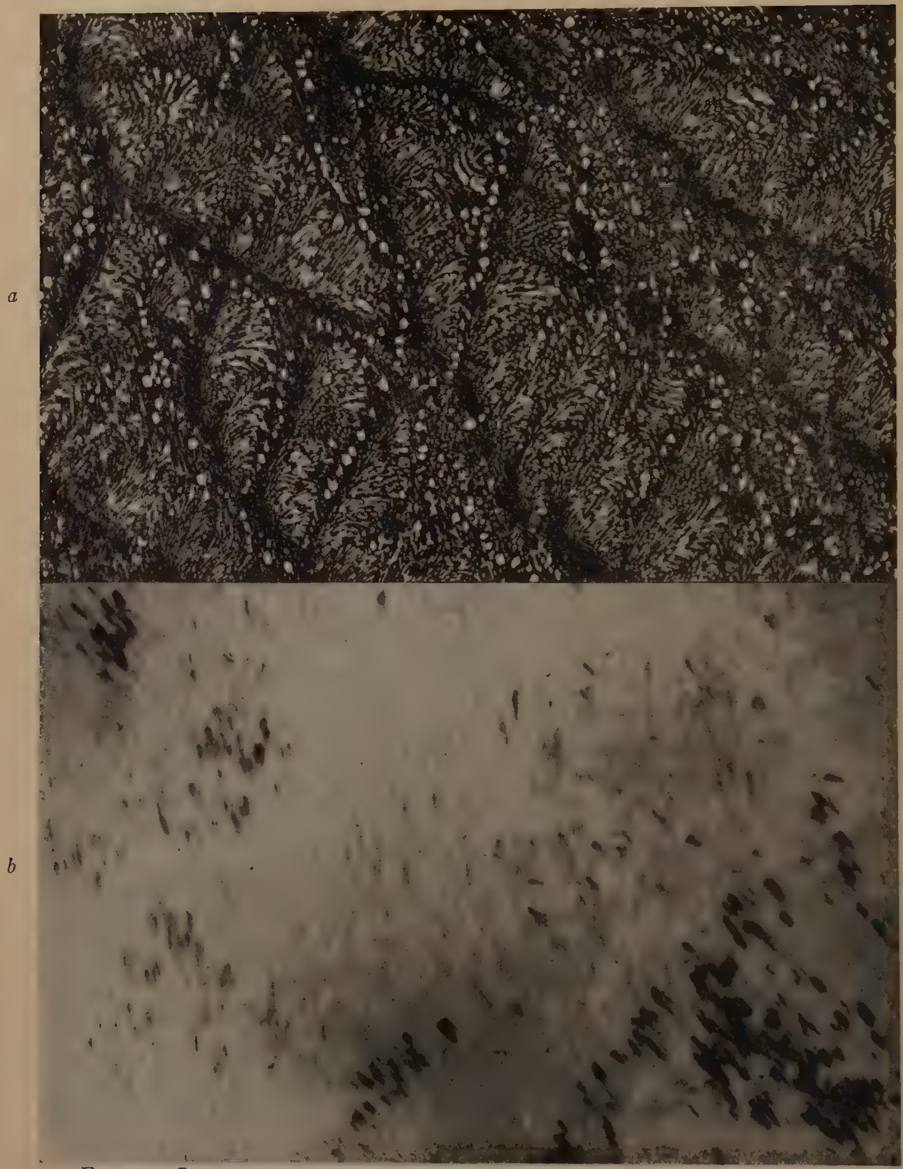

FIG. 40.—INDIUM-TIN ALLOY OF APPROXIMATELY EUTECTIC COMPOSITION. × 100.
Mechanically polished and etched (548-O plate).
a. Photomicrograph.
b. X-ray micrograph of a different area.

beam will be ϕ. If line PQ is drawn perpendicular to OQ, $\cos 2\theta = a/r$, and since $a = c \cos \phi$ and $r^2 = c^2 + t^2$ it follows that

$$\cos 2\theta = \frac{c \cos \phi}{\sqrt{c^2 + t^2}}$$

From the value of θ computed in this way the spacing d of the reflecting planes is obtained from Bragg's law

$$\lambda = 2d \sin \theta$$

where λ is the wave length of the X-rays used. This value (or, better, a series of such values from several strong spots) is compared with lists of spacings in the phases that are thought to be present. Because of the small number of spacings obtainable from micrographs of this sort, it is likely that an unknown cannot be identified with certainty directly from the Hanawalt index.[16]

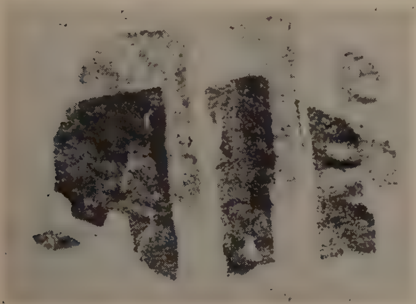

FIG. 41.—IMAGES OF A GRAIN OF CARTRIDGE BRASS ON DOUBLE EMULSION DENTAL FILM. × 50.

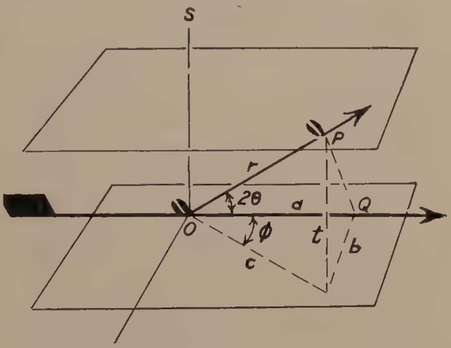

FIG. 42.—DETERMINATION OF ANGLES BY USING IMAGES ON TWO EMULSIONS.

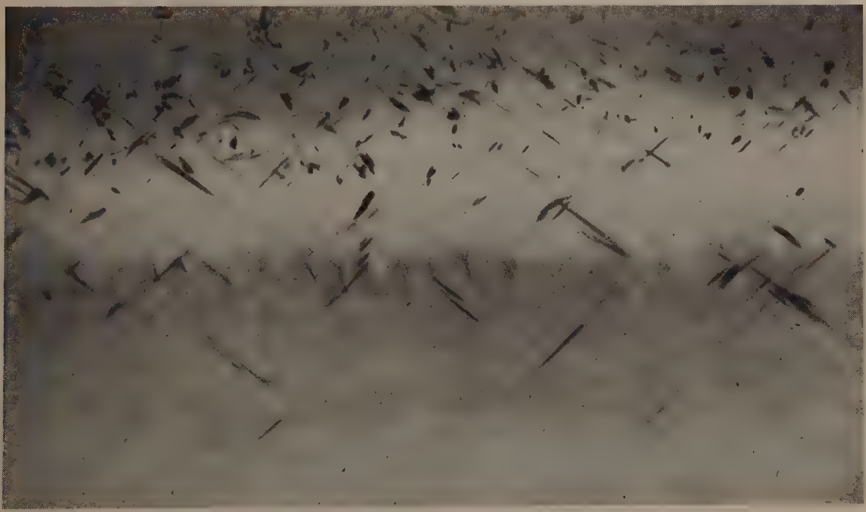

FIG. 43.—STREAKS AT EDGE OF SPECIMEN OF FIG. 35*a*. × 50. Incident beam was vertically downward. 548-O thin-coated plate.

It should be noted that this microanalysis method differs in several essential features from analysis by means of an ordinary X-ray or electron diffraction pattern. In the present method a picture is obtained of the individual crystal or grain that is being identified, while an ordinary powder diffraction pattern is the sum of reflections from all phases present. In the present method equally oriented particles can be identified, but the powder method ignores orientation. Although different in principle, this method has a general similarity to the chemical analysis that is based on microscopic observations of crystals in polarized light.

Another technique for accomplishing the same results is suggested by Fig. 43. A metallographic sample, slightly cold-worked, was in contact with the photographic plate along the top of this picture, and the incident beam was directed vertically downward. Certain of the diffracted rays went out from the specimen almost parallel to the photographic plate, producing long streaks. These are the rays and streaks pictured in a previous sketch (Fig. 29).

The diffraction angle for the atomic planes causing these streaks can be measured with considerable accuracy by bringing the straightest and longest streaks under the crosshair of a microscope equipped with a revolving stage. Measurements on the negative reproduced in Fig. 43 indicate that an accuracy of 0.1° to 0.2° can easily be reached in measurements of the angle between the streaks that extend downward to the left and to the right; this is the angle 4θ (twice the angle 2θ of Fig. 42). Experiments are being continued to determine whether this technique or a modification of it will provide a useful addition to the present types of cameras for the powder method of X-ray diffraction.

Strains from Age-hardening

The tendency in modern theories of age-hardening is to ascribe the increase in hardness almost wholly to microscopic internal strains. The most important strains are thought to be at the interface between the precipitate and the matrix during the early stages of growth of the precipitate.

This is not the place to review the subject or even to summarize the work of Dr. R. F. Mehl and his co-workers in this field. who have found much evidence for the importance of strain; we shall merely survey the potentialities of the present method in this type of investigation.

The experimental results illustrated in Fig. 44 lend support to the strain concept. Fig. 44*a* shows the condition of typical grains in an alloy of copper containing 1.92 per cent beryllium after a negligible aging time in an isothermal bath at 240°C. Fig. 44*b* is typical of the condition after aging at this temperature has increased the hardness from the former value of 32 Rockwell A up to approximately maximum hardness; i.e., 60 Rockwell A. Obviously the grains are distorted in a manner fairly similar to their distortion by cold-work: fragments no larger than 3 to 5 microns are common and the images of all grains are so blurred they can hardly be seen. This corresponds to the blurring of spots that has been noted in ordinary diffraction patterns. There seems no possibility of explaining this result on the basis of the older theory that age-hardening results from a critical dispersion of precipitated particles. The small black dots in Fig. 44*a* are not understood, for while it is natural to associate them with the beginning of aging, it happens that similar marks are found in nonaging materials, as will be discussed later.

Fig. 44*c* differs most interestingly from Fig. 44*b*. It shows that when aging in this alloy is carried out at a high temperature, 550°C., there is much less distortion. A striated appearance of the grains has resulted from the precipitation, but the outlines of the grains are still sharp. This specimen had been overaged until its hardness returned to that of the specimen in Fig. 44*a*.

Aging at an intermediate temperature (400°C.) produced a mottled appearance of all the grain images that indicated a lesser distortion than Fig. 44*b*, in accord-

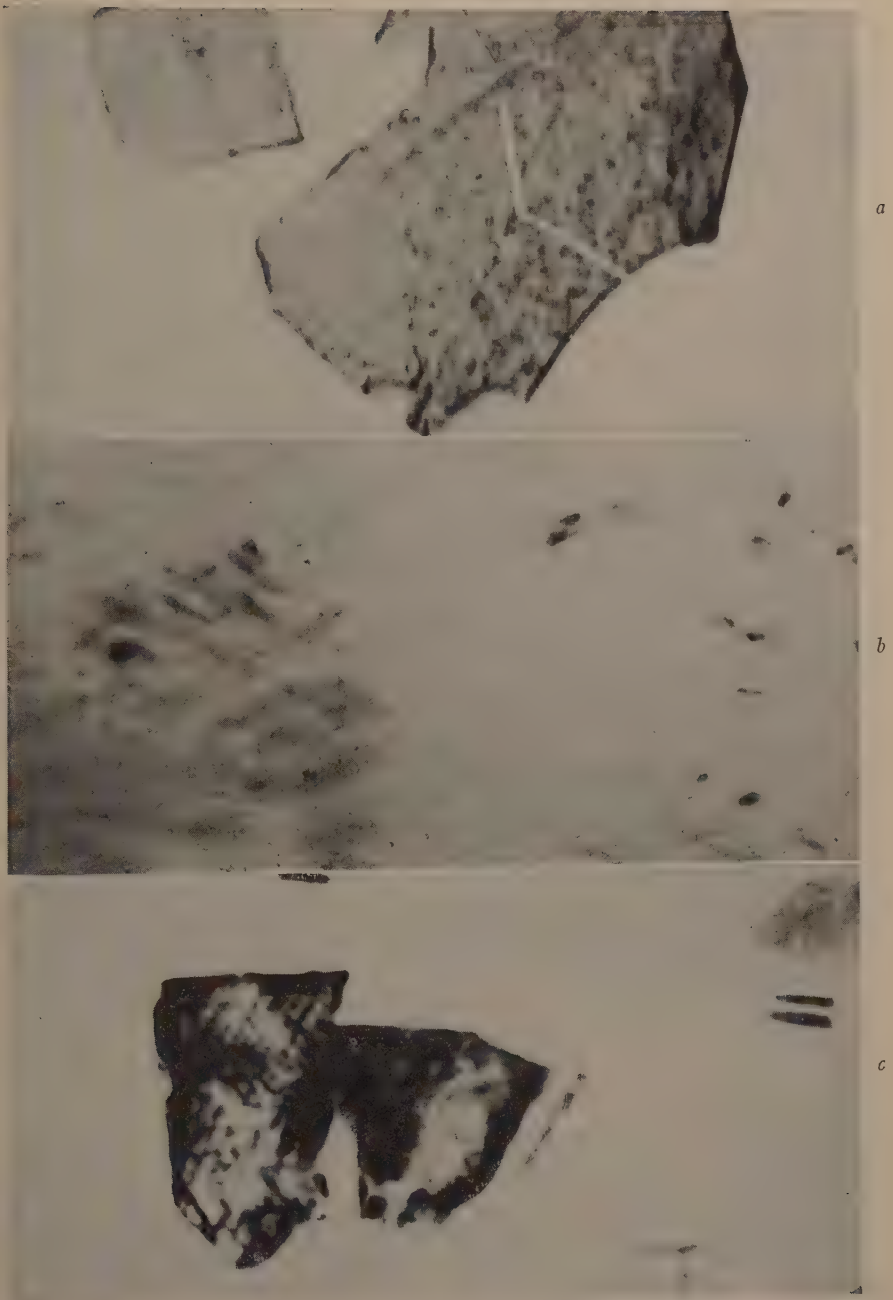

Fig. 44.—Copper-beryllium, quenched from 800°C. into aging bath. Electropolished × 100.

Analysis: 1.92 per cent Be, 0.02 per cent Fe, 0.01 per cent Si.

a. Aged 6 seconds at 240°C. R_A32.

b. Aged 21 hours at 250°C. R_A60.

c. Aged 424 hours at 550°C. R_A31.

ance with a lesser hardening (48 Rockwell A).

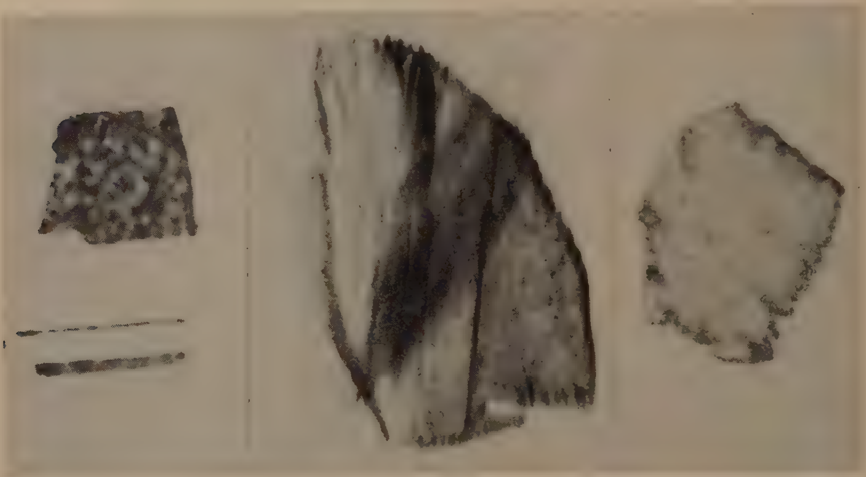
FIG. 45.—COPPER-BERYLLIUM, AIR-COOLED FROM 800°C., ELECTROPOLISHED. × 100.

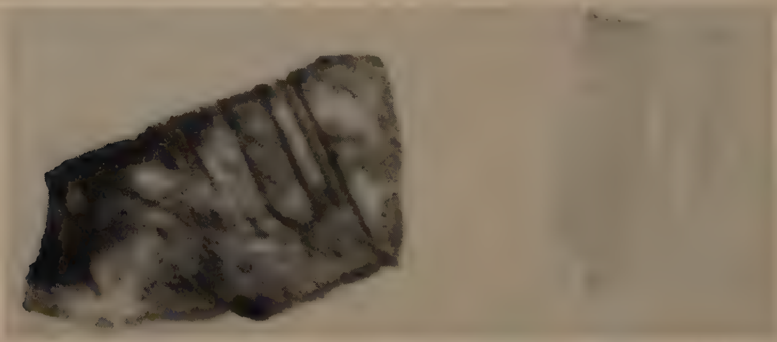
FIG. 46.—COPPER-BERYLLIUM, QUENCHED IN WATER FROM 800°C., MECHANICALLY POLISHED AND ETCHED. × 100.
548-O plate.

There are other features in age-hardening alloys that are open to investigation by this method. Recrystallization at grain boundaries should be easy to recognize when it produces saw-toothed edges on grains. This appears to have occurred in Fig. 45. Close inspection of Fig. 45 reveals black dashes extending in from saw-toothed boundaries. Presumably these reveal the microstrain peaks that are responsible for the continued growth of the recrystallized region. The mottling in the grain at the left of this figure is of unknown significance. It is also possible to show slip lines by these pictures, and it is now recognized that the presence of slip lines in age-hardening alloys exerts a strong influence on the rate of aging and the distribution of precipitate. This is true even when the plastic strain is merely that which results from quenching (see the grain at the lower left of Fig. 46). The slip lines in the center of Fig. 45 may have originated from anisotropic contraction of the grains during slow cooling, for it has been observed recently that even

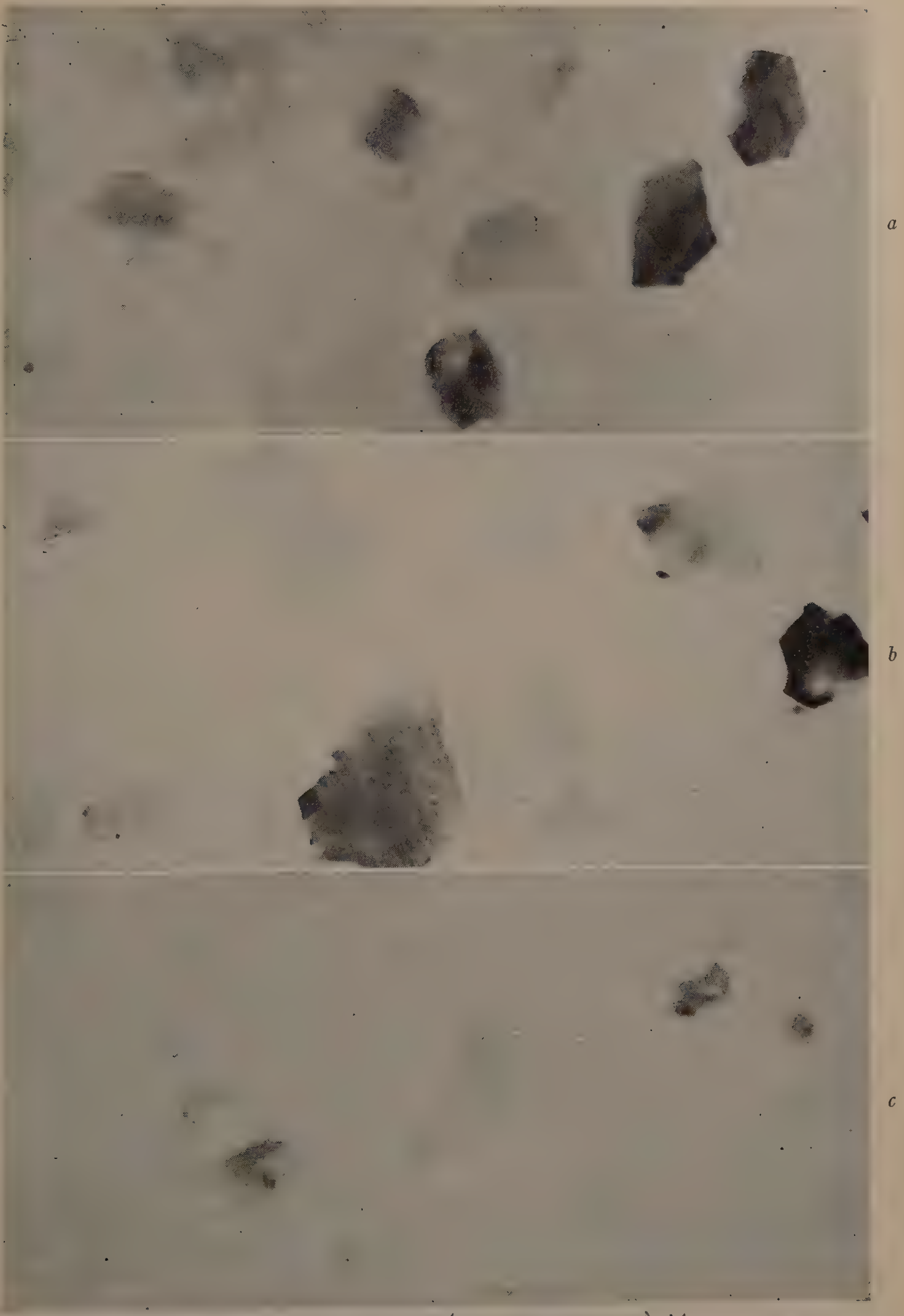

Fig. 47.—Aluminum silver (30 per cent silver). × 50.
a. As quenched from 530°C., Rockwell B-45.
b. Aged 2¼ hours at 225°C., Rockwell B-55 (maximum hardness).
c. Aged 96 hours at 225°C. (overaged).

slow temperature cycles can induce slip in polycrystalline tin, cadmium and zinc.[17]

A very slight blurring of diffraction spots occurs when aluminum-silver alloys are aged, and the corresponding blurring may be seen in the images of Fig. 47. The aluminum-rich alloys of this system harden but little (Fig. 47*a* is at 45 Rockwell B, Fig. 47*b* at 55), despite a relatively great amount of precipitate. In the grains at maximum hardness (Fig. 47*b*) there is an interesting fine structure of gray and white lines that extends entirely across the grains in parallel sets. Whether these lines are primarily the result of slip or are some precipitation effect has not yet been determined.

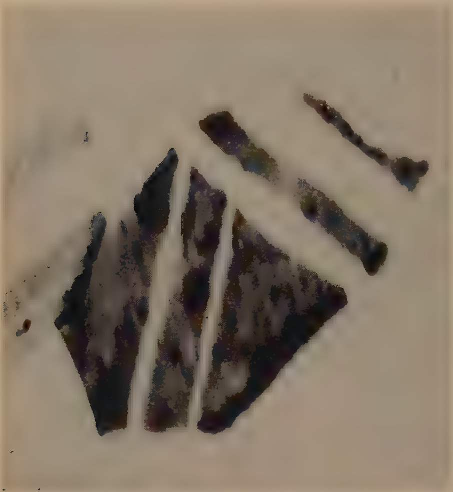

FIG. 48.—RECRYSTALLIZED CARTRIDGE BRASS, REPEATEDLY POLISHED AND ETCHED. × 50.

The Hardness of Solid Solutions

One would expect that the hardness of solid solutions would be connected with distortions on a scale too fine to be registered on the present pictures. Yet this theory should not be accepted without experimental verification, since other causes of hardening have shown themselves capable of causing great changes in the micrographs.

Several solid solutions are represented in the present illustrations. The iron-silicon alloy of Fig. 18*b* shows, in the gray area at the bottom of the print, many small black dots that are not specks of dirt on the specimen or the negative. They appear again at higher magnification in Fig. 10, where it can be seen that their size lies in the range from 10 microns down to the limit of resolution of the image. There are peculiar dots also in Fig. 44*a*, probably not connected with precipitation. Short dashes are found in recrystallized brass (Fig. 48), even after great care had been exercised in the metallographic preparation.

In all of these presumably strain-free materials the dots do not have the length that would classify them as slip lines, yet they have the reflecting power of the strained regions at slip lines. They must therefore reveal some natural imperfection originating from recrystallization or originating earlier and surviving recrystallization, or perhaps they represent an inherent characteristic of a solid solution. If they exist in great numbers, perhaps below the present resolving power of the pictures, they can be at least one cause of the hardness of solid solutions.

When an alloy changes from the random arrangement of atoms on lattice points that is known as a solid solution to the ordered array that is called a superlattice, there must be profuse distortion, particularly if the ordering starts simultaneously at many different nuclei that are differently oriented with respect to each other and if the ordering changes the crystal lattice to one of lower symmetry. The superlattices capable of the greatest hardening by heat-treatment are the ones in which a change of the crystal lattice accompanies aging, like the change from cubic to tetragonal.* It is in this class of superlattices, then, that alterations in the X-ray micrographs can be predicted with some confidence.

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* This generalization was discovered by A. A. Guy during his research at this laboratory.

Summary

This lecture presents a new microscopy of potential value in physical metallurgy and in other fields and is a frank attempt to promote its use by others. The essential elements of the method are a fine-grained photographic plate placed in contact with or very close to the specimen to be examined, and a beam of characteristic X-rays striking the specimen. Images formed on the plate by diffraction can be enlarged to useful magnifications up to 100 or perhaps to 250 diameters.

These X-ray diffraction micrographs show the places where inhomogeneous strain is concentrated. Along planes where slip has occurred throughout the interior of crystals and polycrystalline grains there is a local bending or rotation of the crystal lattice. This increases the efficiency of X-ray reflection and causes a dark line on the photographic plate. Combined with goniometer measurements, these micrographs show that local rotation at slip lines is less than 0.1° (in slightly deformed ferrite) and is confined to a layer 3 microns thick or less, whereas rotation at the boundaries of deformation twins in ferrite lies in the range 0.5° to 1°.

The sizes and shapes of polycrystalline grains are nicely shown. Irregularities on the surface, such as etch pits, show clearly when they cast shadows in oblique radiation. A small amount of plastic deformation causes a fragmentation of the image of each grain into an assemblage of dots presumably representing microstrain peaks and perhaps grain fragments. Deformation bands can be recognized in the images of grains, as well as deformation twins, annealing twins, included grains, and distortion from scratches and cutting tools. Higher deformations produce long streaks in which internal detail cannot be resolved, and ultimately destroy all images.

The cold-worked structure persists throughout the recovery period during annealing, and disappears only when it is devoured by strain-free recrystallized grains. Recrystallized grains are easily seen and distinguished from slightly cold-worked grains.

The imperfections of cast grains are clearly shown, not only in alloys where coring is present but also in pure metals. Clusters of similarly oriented crystals in eutectics and eutectoids can be seen.

By measuring the directions of the diffracted rays from individual microconstituents, the method provides a means of indentifying them, and makes microanalysis possible on individual particles.

Age-hardening in some alloys causes a fragmentation of the grain images much like cold-work. Recrystallized areas that form along grain boundaries during cold-work are seen, together with evidences of strain adjacent to the recrystallized area.

Recrystallized solid solutions have local imperfections at scattered points, and distortion in the images is predicted for superlattices in which a change of lattice symmetry accompanies ordering.

Appendix I.—Exposure Data and Techniques

All X-ray films are too coarse grained to permit great enlargement. Dental film, however, is useful in quick preliminary exposures; its graininess at 50 diameters is indicated by Fig. 41. For better results at magnifications of 25 and 50, a spectroscopic plate is recommended, such as Eastman's 5-O (or V-O). For the highest resolving power I have used Eastman's Experimental 548-Ortho thin-coated spectroscopic plates or the same plate in a coating of regular thickness. Somewhat below these in resolving power are Eastman's 548-O spectroscopic plates. Approximate exposure times can be judged from Table 1; exact values are not listed because they depend upon whether interest is centered in the strong or the weak reflections, and also upon the distance from the X-ray tube to the specimen, degree of cold-work, etc.

TABLE 1.—*Approximate Exposure Times with Cobalt Radiation*

Specimen	Type of Emulsion	Suitable Exposure Times	Example, Fig. No.
Mg............	V-O	5 to 10 min.	37
Al.............	V-O	⅙ to 2 hr.	22, 26
	548-O	1 to 3 hr.	34
	548-ortho	2 to 12 hr.	
Fe, Fe-Si.......	Dental	1 to 5 min.	3
	V-O	5 to 25 min.	20
	548-O		23, 28
	548-ortho	10 to 17 hr.	35
Cu, Cu alloys..	Dental	2 to 5 min.	41
	V-O	¼ to 1 hr.	38
	548-ortho	2 to 12 hr.	46
Pb.............	V-O	2 to 5 min.	1
	548-ortho	2 to 10 hr.	

The plates were developed for 3 to 9 min. in D-19 developer, dipped in a short-stop bath, fixed, washed for 20 min. or more, rinsed in a vigorous stream of water and sometimes sponged very delicately to remove dirt, then dried in a dustproof enclosure (sometimes with the aid of heaters). Contrast and density in the negative increases with development time, and if the final image is too dark for suitable enlargement the negative is reduced with Farmer's reducer. In hot weather Defender's fine-grained developer "777" was successfully used.

If one is anxious to see the results of an exposure immediately, the image can be viewed in a microscope when the plate is still wet from the washing, or even when the negative is immersed in a Petri dish containing the fixing solution. When impatience reaches a still higher pitch, the plate can be viewed with yellow light in a microscope while the plate is in a Petri dish containing the developing solution.

Excellent enlargements may be made by using a petrographic or a metallurgical microscope with a long-focus objective, and relying on the poorer lenses of an ordinary photographic enlarger for the lower magnifications or for wider fields of view. It is sometimes convenient to project the enlarged image directly on bromide paper, but to make the reproductions resemble the original negatives the present reproductions have been made by projecting on metallographic plates and printing from these. When some areas of the negatives are very dark, the unexposed parts should be blocked out with black tape or with opaque. Some dodging in printing is necessary when the background is of uneven density. In one instance, Fig. 19, a positive was made on 548-O film by contact printing, and the positive was projected in an enlarger. This is a less expensive process but doubtless is inferior in resolving power, and is difficult to carry out without an excessive amount of dirt appearing in the final image.

The distance from X-ray tube to camera for nearly all polycrystalline studies was 15 to 30 cm., and customarily two cameras were placed in the beam from a single window of the tube, wide slits being used at the window to limit the beam. Single-crystal exposures were made at 26 cm. from the tube with a slit 0.2 mm. wide placed normal to the photographic plate at a distance 2 cm. from the tube.

Appendix II.—Electron Diffraction Microscopy

An obvious question to be answered is why the X-ray diffraction methods presented here cannot be extended to the field of electron diffraction (or, for that matter, to the diffraction of material particles). A photographic plate placed very close to a diffracting specimen should receive diffracted electrons and yield an image of the diffracting power over the surface in the same way that it does for X-rays. There would be at least two important differences, however.

Electrons that have been accelerated by voltages in the usual range (10^4 to 10^5 volts) possess a very short wave length and hence diffract at very small angles. All of the strong reflections will lie within a few degrees of the incident beam. This would make it more difficult to shield the photographic plate from the direct beam and more difficult to avoid distortion in the diffracted image. The extremely small angle of incidence with which the diffracted rays would strike the photographic emulsion, if the emulsion were parallel to the incident beam, could cause a serious loss of resolution in the image; whereas if the plate were turned so as to lie perpendicular to the incident beam all crystal images would be very greatly foreshortened—an equiaxed grain on the surface of a specimen would produce an image roughly $1/50$ as wide as it was high. Perhaps these difficulties could be overcome by employing lower voltages, thereby increasing the wave length of the electrons and their diffraction angles, but this approach to the problem would not be without its obstacles also.

A second important way in which electrons differ from X-rays is in their lack of penetrating power. Diffraction takes place within a few tens or hundreds of angstroms from the surface. When an ordinary electron diffraction pattern is made by the surface reflection method probably only the projecting peaks of the roughened surface contribute to the pattern and an electron diffraction micrograph would show only these peaks. The distribution of etch pits on the surface of the specimen would therefore be very important, and unless the etch pits were small there would be poor detail in the image. As in all electron diffraction work, the pictures would be extraordinarily sensitive to any contamination of the surface by condensed vapors, oxides and the like.

It appears at this time, therefore, that the superior "resolving power" of electrons, which is made use of so effectively in the electron microscope, could not easily or effectively be substituted for X-rays in any camera such as has been discussed here. However, there have been several observations of images in electron microscope pictures that are essentially the same as these, since they register individual particles of a crystalline powder by the Bragg reflection mechanism.[18] Research by the use of these reflections should make it possible to extend some of the present studies into the realm that is accessible only by the electron microscope. For example, if slip lines can be recognized in the images of cold-worked grains, a much more precise determination might be obtained of the width of the distorted region at a slip line than is possible by X-rays.

Appendix III.—Penetration Effects

Characteristic radiation from cobalt, having a wave length of 1.78Å., is able to penetrate 40 microns of aluminum before being reduced to half value by ordinary absorption. This raises the question of how the high degree of clarity was obtained in X-ray micrographs of aluminum and magnesium with this radiation. One answer lies in the fact that the sheet specimens used in the preparation of the preceding micrographs were nearly parallel to the X-ray beam, so the beam penetrated only about 4 microns below the surface in going 40 microns through the aluminum. Therefore, the majority of the reflected rays arise from a layer at the surface that is hardly deeper than the dimensions of the smallest details of the image. It appears that with the technique in its present state there are four limitations on the resolving power, all of which put the limit at about 1 to 5 microns: (1) penetration into the sample, (2) geometrical factors expressed in the first equation of the text, (3) the resolving power of the photographic emulsion, and (4) the natural imperfection of the diffracting crystal lattice.

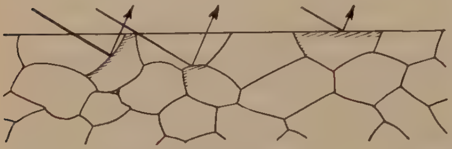

FIG. 49.—PENETRATION EFFECTS IN LIGHT METALS.

Strongly reflecting regions indicated by crosshatching.

The question of penetration, however, involves more than a consideration of the ordinary absorption coefficient, for the attenuation of the incident beam is increased greatly when a crystal reflects a strong beam. Using the theory for primary extinction in a perfect crystal,[19] the effective absorption coefficient in a reflecting crystal may be estimated by the approximate formula

$$\mu_e = \frac{2Fe^2n\lambda}{Zmc^2 \sin \theta}$$

where F is the structure factor for the reflection concerned, n is the number of electrons per cubic centimeter, e is the charge in the electron, λ is the wave length, Z the atomic number, m the mass of an electron, C the velocity of light and θ the Bragg angle.

For reflections of cobalt radiation from aluminum at 2θ near 90° this predicts a penetration of only 0.6 micron before the ray is reduced to half intensity. Other figures for reflection at $2\theta = 90°$ are given in Table 2.

TABLE 2.—*Half Value Thickness for Perfect Crystals*

Radiation	Specimen	Half Value Thickness in Microns	
		Not Reflecting	Reflecting
Co	Cu	~10	0.1
Co	Al	40	0.6
Mo	Al	510	1.1

These computations suggest that in the lighter metals the images are formed as in Fig. 49, not only by grains on the surface, but also by grains slightly below the surface. The rays should penetrate rather easily through nonreflecting grains and be abruptly diverted by reflection in the outer skin of the first strongly reflecting grain. Hence the reflected images should be built up from material distributed as indicated by the crosshatching. Penetration effects would be more prominent with the lighter metals and with greater angles of incidence of the rays on the specimen.

In cold-worked grains many of the nonparallel rays should penetrate relatively easily through unstrained portions until they encounter strained material, and then abruptly reflect (cf. discussion of Fig. 13 in the text). It should be possible, therefore, to have conditions in which strained material could be "seen" at appreciable depths below the surface of "transparent" grains; such conditions are met in Fig. 50, with molybdenum radiation and an aluminum specimen. This picture was, in fact, formed by rays that passed entirely through a thin sheet of the sample used for Fig. 32*b*, since the sheet was tilted in the reverse from the usual manner. All striae are relatively long, which seems to confirm our view of their origin.

The facts that have been presented in this lecture should be considered in any future research on the physics of X-ray diffraction. Studies in the past have dealt with *average* values of extinction and reflecting power; now it is clear that important variations occur on a microscopic scale, and it should be possible to determine these values at individual points on the crystal. For example, a more precise statement can now be made of the nature of the crystals used; slip lines introduced by cleavage can be readily detected and a better idea of natural imperfections can be obtained.

Acknowledgments

So many friends have aided me in this work it seems appropriate to devote an entire appendix to acknowledging their assistance. The fruitful work that was conducted during the summer of 1944 by Dr. Potvin has already been mentioned. I acknowledge with pleasure also the helpful discussions of the manuscript by various faculty members, especially Professors R. F. Mehl and F. Seitz, and of my ink and watercolor drawings by Prof. Roy Hilton. The patient and skillful work of Mrs. Kathleen Wells, who made the enlargements and prints, is particularly appreciated. The Eastman Kodak Co. rendered valuable assistance by furnishing special emulsions and advice as to their characteristics. Certain X-ray diffraction equipment was kindly lent by the Picker X-ray Co. The list of those who prepared specimens or furnished research material or photographic equipment is long: W. A. Anderson, G. Ansel, H. W. Cobb, D. K. Crampton, H. E. Elliot, M. Gensamer, A. A. Guy, A. H. Grobe, C. T. Haller, M. Hawkes, C. Lacey, L. H. Miller, Edna Matson, E. W. Palmer, G. E. Pellisier, F. N. Rhines, J. K. Stanley, F. E. Swindells, F. S. Swann, L. Susini, Wilma Urquhart and Helen Uramey. I cannot close without a word of appreciation for the forbearance of my family and my friends during the time that so much of my attention was centered on this research, and for their encouragement.

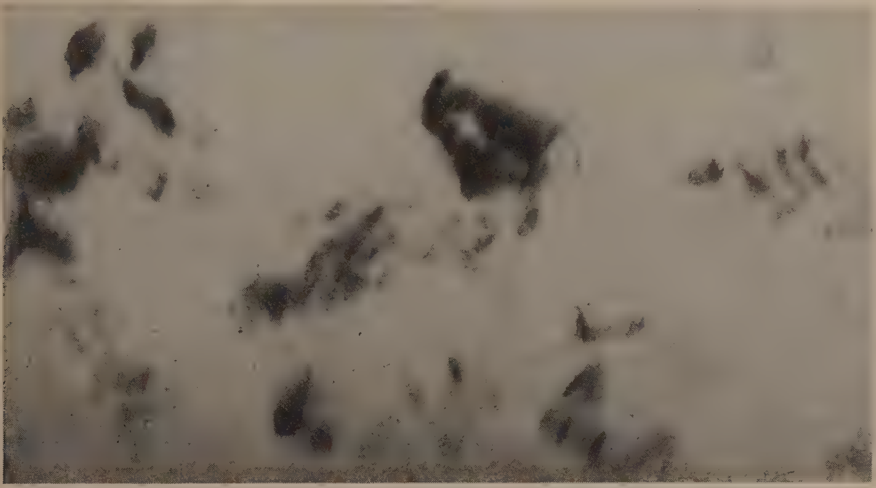

Fig. 50.—High-purity aluminum strip, elongated 5 per cent. Electropolished. × 100. Picture formed by molybdenum radiation transmitted through specimen.

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Fundamental Principles Involved in Segregation in Alloy Castings

By R. M. Brick,* Member A.I.M.E.

(New York Meeting, February 1944)

Segregation can occur only in cast alloys that solidify over a range of temperatures with a difference in composition of liquid and solid phases within this range (ignoring monotectic systems and chemical reactions as in rimming steels). Thus a pure binary eutectic alloy should show no segregation unless undercooling occurs for one of the solid constituents of the eutectic; e.g., chill-cast Al-12 per cent Si alloys.

The phasial condition implicitly described above—solidification over a range of temperatures with a compositional difference between solid and liquid—is found in nearly all solid solutions or combinations of solid solutions and eutectics. Metastable conditions of solidification of these types of alloys cause *coring;* i.e., a difference in composition between the center of a dendrite and its periphery. This composition gradient can be detected usually only by microscopic examination of etched structures; it is a "micro" effect. The gradient of more immediate industrial concern is that between the center of a cast section and the surface layers. This gross (macro) effect is usually determinable only by sampling of the casting at different points, with chemical analyses of each sample. If the compositional difference is of the same type as in coring, the first parts to freeze being enriched in higher-melting-point constituents, and vice versa, the effect is called *normal segregation.* When what is apparently the first part of the casting to solidify shows a higher concentration of low-melting-point constituents, the effect is called *inverse segregation.* These macro effects are quite separate from the micro effect, coring, yet the latter must be described first because it is an essential part of the picture.

Coring

Solid Solution, Ni-Cu

The nickel-copper phase diagram is reproduced in Fig. 1*a*, in which the solid lines represent the *equilibrium liquidus 1, 3, 7 and solidus 2, 5, 8*, and where the vertical *1*, *4*, *8* represents a 55 per cent Cu alloy. Upon moderately rapid solidification, the first dendritic axes of composition *2* (see Fig. 1*b*) start to form at a temperature somewhat under *1*. Solidification continues by growth of the dendritic nuclei, but at temperature *4* the increment solidifying is of composition *5*. The rapidity of this crystal growth prevents diffusion of nickel and copper atoms from adjusting the composition of the entire dendrite at *5*, which it would be under equilibrium conditions. The *average composition* of a specific dendrite, or the entire solid phase, at temperature *4* might be that indicated

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by point *6*. The alloy should be completely solid at temperature *8* but this is possible only if the average composition of the solid phase is that shown by *8*; in other words, if the dendrites are homogeneous and equilibrium conditions have been attained.

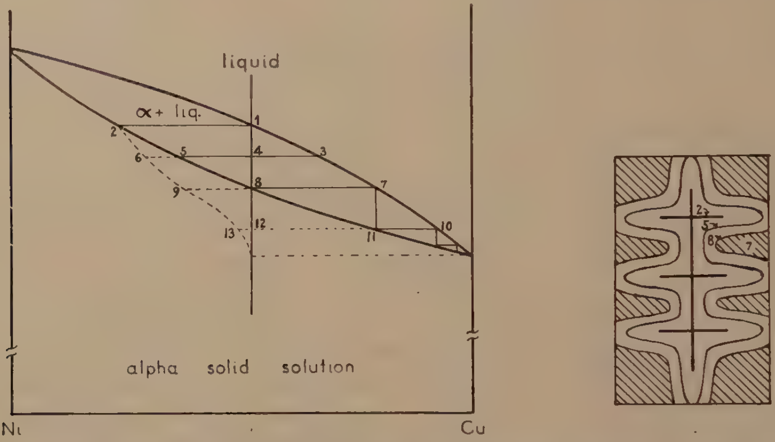

FIG. 1.—NICKEL-COPPER PHASE DIAGRAM (*a*) AND ACCOMPANYING DENDRITIC CORING EFFECT (*b*) AT TEMPERATURE *9-8-7*.

Dashed line 2-6-9 shows metastable displacement of solidus upon undercooling; e.g., during solidification of a 55 per cent Cu chill casting.

The coring effect, however, requires the average dendritic composition to be approximately that shown by *9* and there remains considerable liquid, $\left(\frac{9-8}{9-7}\right) 100$ per cent, of composition *7*.* Since under conditions of fairly rapid solidification little diffusion may occur, this liquid freezes independently, in a chemical sense, of the dendrites already present, although physically the liquid solidifies by growth of these crystals. Under these circumstances, it can readily be seen that the final liquid to freeze may be practically pure copper at a temperature of 1083°C.

Another way of showing this is to follow the line showing the actual average composition of the dendrites, line *2, 6, 9, 13*—or the *metastable solidus* for the 55 per cent Cu alloy which asymptotically meets the composition vertical. When the solid phase has the same composition as the total alloy, no liquid can remain. Thus by the construction of Fig. 1 and the assumption of nearly zero diffusion, a cored structure may be postulated where the dendritic axes contain about 80 per cent Ni and the interdendritic fillings are almost pure copper. Fig. 2 shows a typical chill-cast cupronickel dendritic structure. Here, the nickel-rich and copper-rich portions may be distinguished on the basis of continuity; the last (copper-rich) portion to freeze, being interdendritic, is continuous.

Solid Solution and Eutectic; Al-Cu, Fe-W-Cr-C

There are many alloys such as the industrial Al-4 per cent Cu (Alcoa 195) that theoretically should freeze as solid solutions, from reference to the appropriate phase diagram (Fig. 3), but that actually usually show some eutectic in the cast microstructure (Fig. 4). The explanation of this effect is implicit in the description of coring in Cu-Ni alloys and is diagrammatically shown in Fig. 3 by a similar metastable solidus construction. The liquid in a eutectiferous system may be enriched, as it is here, in the higher-melting-point element without the coring being considered as inverse.

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* The assumption is made here that liquid diffusion will be sufficiently rapid to equalize the composition of the liquid. This is not actually true, but it is almost impossible to obtain experimental evidence regarding the extent of "coring" in the liquid phase (see p. 70).

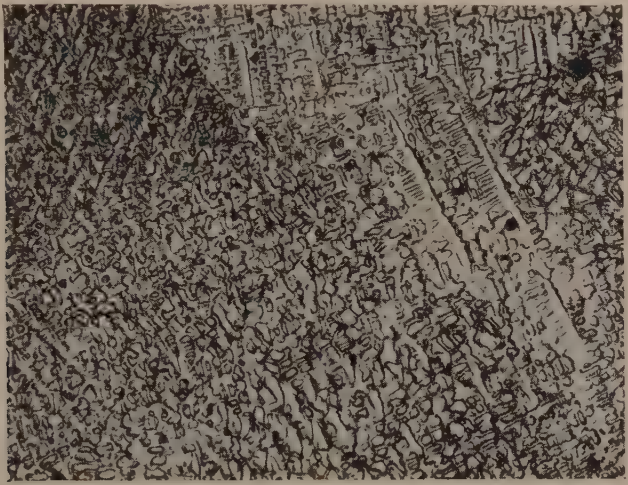

FIG. 2.—CORED DENDRITIC MICROSTRUCTURE OF CHILL-CAST CUPRO NICKEL. × 50.

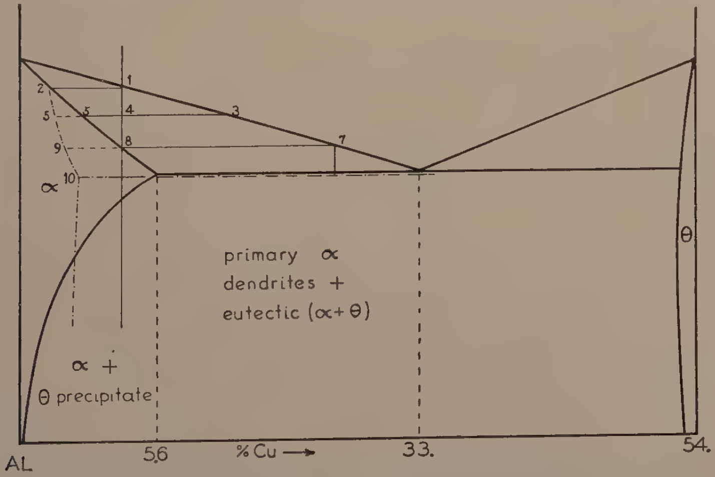

FIG. 3.—ALUMINUM-COPPER PHASE DIAGRAM LABELED ACCORDING TO STRUCTURES SHOWN BY CAST ALLOYS, ASSUMING EQUILIBRIUM IS MAINTAINED.

Dash-dot lines show effect upon phase field boundaries of undercooling during solidification of a 4 per cent Cu alloy casting.

Again, at the temperature where the alloy should theoretically be solid, *8*, coring causes the actual average dendritic composition to be about that shown by *9*, and some liquid (*9*-*8*)/(*9*-*7*) 100 per cent, of nearly eutectic composition remains. Since fairly rapid solidification is again assumed, the liquid may undercool somewhat but it freezes only slightly below the eutectic temperature (548°C. in a pure, binary alloy) and the alloy shows some eutectic structure. In Fig. 4, the theta phase does not show its usual lamellar eutectic structure but this is explained by the preferred nucleation effect of the primary alpha dendrites upon which the alpha of the eutectic freezes, leaving massive theta.

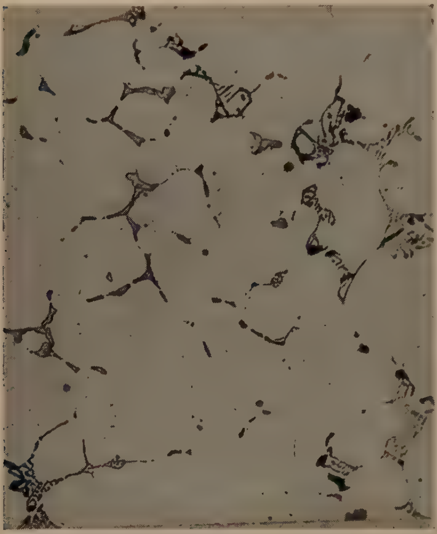

FIG. 4.—ALUMINUM ALLOY 195 AS CAST. × 100. Composition of alloy is Al + 4 per cent Cu + Fe + Si impurity. Clear, outlined particles are eutectiferous theta; black "chinese script" is Al-Fe-Si impurity compound.

That this effect is not confined to nonferrous alloys is shown by Fig. 5, a photomicrograph of a cast and annealed alloy whose major components are Fe, 7 per cent W, 7 per cent Cr and 0.5 per cent C. A pseudobinary phase diagram for this alloy at temperatures above 1550°F. would be similar to Fig. 3 except that for alpha there should be substituted alloyed gamma; for theta, a tungsten-chromium carbide, and finally the eutectic "horizontal" should end on the left at about 0.6 per cent C. Thus the cast alloy should show no eutectic, theoretically, but when an attempt was made to substitute castings for forgings of this alloy, the annealed castings showed massive interdendritic carbides (Fig. 5) of eutectiferous origin. Their embrittling tendency is not obliterated by the hardening heat-treatment although the desired hardness of Rockwell C 60 is readily attained. Fig. 6 shows that the austenitizing treatment failed to dissolve all of the massive interdendritic carbides. In addition, it brought out the coring in the original austenitic dendrites beautifully; since the dendritic cores were low in the important alloy constituents Cr, W and C, these sections transformed completely to martensite on the quench and the subsequent tempering operations blackened this structure while the interdendritic areas, enriched in the alloying constituents, formed a much more stable austenite, resistant to the martensite transformation and therefore unaffected by tempering. In this alloy, then, as in the somewhat comparable high-speed steels, forging is required to break up the interdendritic carbides, although even extensive hot-working does not eliminate austenitic coring; it merely changes a dendritic structure to a banded structure (Fig. 7).

GRAVITY SEGREGATION

Three types of segregation caused by a gravity separation of phases of different densities may be distinguished. The first is a segregation occurring upon quiet *melting* where the liquid first formed is much lighter or much heavier than the skeletonal solid crystals remaining. This can occur upon melting of an Al-Cu alloy[1] that had solidified in a pot—accidentally or for degassing purposes. The enrichment in copper of the lower part of the melt may be eliminated simply by stirring.

A second form, occurring upon solidification, is based on the same fundamental effect. A casting of a slightly hypoeutectic or hypereutectic alloy, which contains only a few primary crystals whose density is considerably greater than that of the

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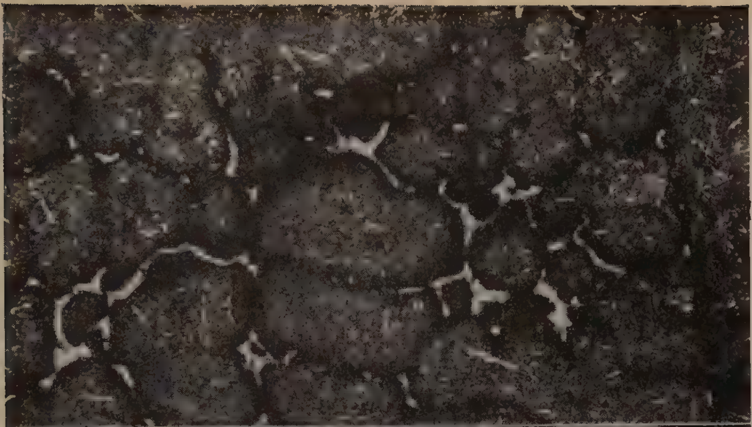
[1] References are listed at the end of the paper.



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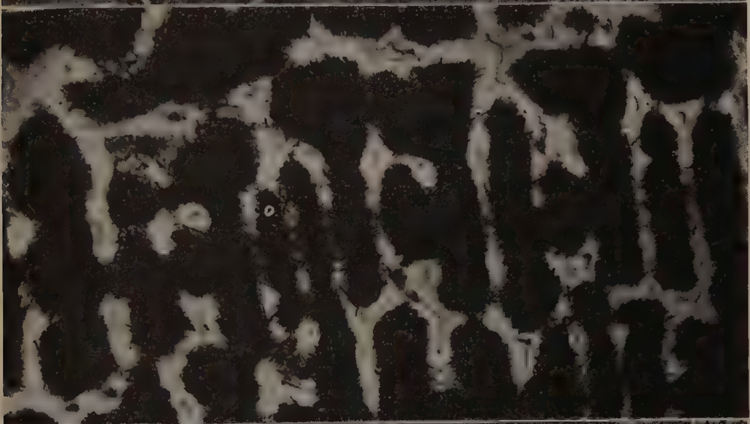

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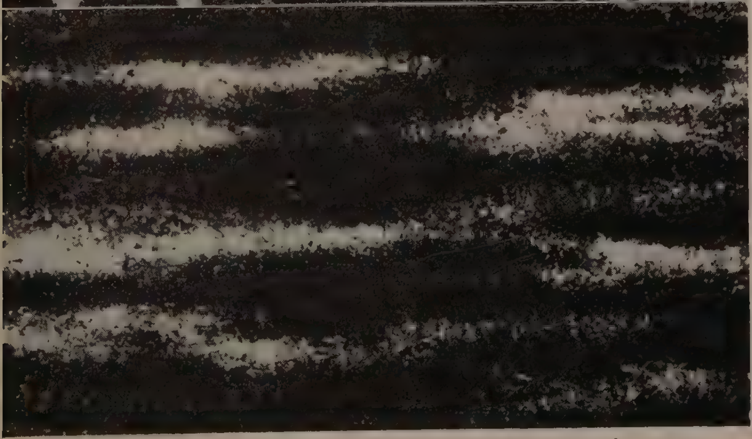

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FIGS. 5 and 6.—CAST STEEL (7 PER CENT W, 7 Cr, 0.5 C). × 100.

Fig. 5.—Annealed condition. Dendritic cored structure of alloyed ferrite and carbide (formed from cored, primary austenite dendrites) with massive interdendritic, eutectiferous carbide (white).

FIG. 6.—Hardened and tempered condition (Rockwell C60). Black, tempered martensitic needles occupy former cored gamma dendrites; white retained austenite surrounds residual (undissolved) massive, interdendritic eutectiferous carbides.

FIG. 7.—WROUGHT STEEL (7 PER CENT W, 7 Cr, 0.5 C) IN HARDENED AND TEMPERED CONDITION. × 100.

Dendritic structure converted to banded structure by hot-working; forging broke up massive carbides but did not eliminate coring; it merely changed the physical distribution of cored areas.

eutectiferous liquid remaining, can show marked gravity segregation. For example, it is difficult to get a uniform dispersion of small, primary Sb crystals in a Pb-20 per cent Sb alloy; these lightweight, rhombohedral crystals, not held in place by interlocking of dendritic arms, tend to rise in the heavier eutectiferous (12 per cent Sb) liquid. Trouble of this type is worst, naturally, in heavy sections that solidify relatively slowly.

The third type of gravity segregation is that found in monotectic alloys where the two liquids, existing over a limited temperature range, are of markedly different densities. The commonest example of this effect is found in the Cu-Pb system, for alloys containing from 38 to 92 per cent Pb. Alloys of this type are particularly well adapted for fabrication by powder metallurgy methods.

NORMAL AND INVERSE SEGREGATION

If solidification took place by the growth of dense, impermeable crystals (i.e., layers containing no residual liquid and with no interdendritic channels) in accordance with temperature gradients within a liquid alloy cast in a cold mold, and if little diffusion occurred, all segregation would be of the normal (coring) type and with a tremendously greater disparity in composition from surface to center than is actually ever found; i.e., all segregation would be of magnitude comparable to microsegregation or coring. However, the dendritic form of crystallization seems to be universal and, with the accompanying continuity of interdendritic channels, other physical forces that can influence the movement of low-melting-point liquid through these channels become significant; viz.: (*A*) internal gas pressure, (*B*) contraction accompanying the phase change, liquid to solid, and cooling of the solid.

Other forces have been advanced as general explanations for inverse segregation. For example, crystallization pressure[4] is certainly not a sole cause, although it may cooperate with contraction forces in certain cases. Two growing dendrites might force each other apart and thus create a low-pressure area with a resultant flow of enriched liquid to this point. Certainly, the dendrites could not force each other apart in the surface zone of a solidifying casting when probably 90 per cent of this zone is solid. The same argument may be applied to the suggestion of Watson[3] that primary dendrites migrate from the mold wall to be replaced by low-melting-point liquid. Other causes advanced by different individuals are reviewed by Vaughn[4] and critically discussed in so many other articles (e.g., refs. 1, 5, 6) that it seems unnecessary to cover them here.

In the absence of either of these forces, *A* or *B* above, presumably there would be no macrosegregation since the statistical distribution of coring would be uniform. Only one of these forces, *A*, can be clearly demonstrated to cause a specific form of segregation. Hydrogen absorbed by liquid tin bronzes, for example, is not removed by the deoxidizer. Solidification of the cast bronze starts in the usual manner; copper-rich dendrites form a shell and residual liquid, enriched in tin, remains in the interdendritic channels and liquid center section. This liquid is also enriched in hydrogen until at a certain degree of supersaturation gaseous bubbles form and expand, forcing the tin-rich liquid through interdendritic channels, and in extreme cases extruding it into the contraction opening between mold and casting.[2] The resultant exudations raise the average tin content of the surface above the average for the alloy—thus inverse segregation has occurred. This form of difficulty is readily detected as to cause and may be avoided by an oxidation treatment of the liquid prior to deoxidation and casting.

The most important general cause of segregation, then, is now generally agreed to be: (1) the compositional effect of coring; (2) the presence of interdendritic channels filled with enriched liquid, and, finally, force B, contraction of dendrites creating a low pressure in the channels and an accompanying flow of liquid. This statement is based on the facts that inverse segregation has been found in slush castings where gas pressure is certainly not a factor,[7] in degassed Al-Cu alloys solidified under a vacuum[10] and therefore free of gas-evolution factors, in single crystals where neither gas pressure nor crystallization pressure presumably would be operative,[1] and that liquid and solid phases in the proper temperature range can be separated by interdendritic flow.[6] However satisfactory the statement of coring plus interdendritic flow may seem, it fails to answer some of the most important questions relating to segregation.

Aluminum alloys, containing approximately 4 per cent Cu—of which there are many, including the Alcoa 195 casting alloy and the duralumin-type wrought alloys—usually show inverse segregation, but by changing the rate of solidification in either direction, more or less rapid, the extent of inverse segregation diminishes and may change to the normal type.[1,5,8–10] The diminution upon slower solidification could be explained by more complete diffusion, therefore less coring and less enrichment of the liquid in solute atoms. The diminution upon more rapid freezing would have to be explained by the channels becoming cold so quickly that interdendritic flow is largely blocked. That this is the case is indicated by the increase in shrinkage porosity with increase in solidification rate. However, Masing[5] has found two peaks in degree of inverse segregation with increase in cooling velocity. He was not able to offer an explanation of these results; nor, for that matter, has anyone else!

Omitting exudations caused by gas pressure and compositional changes effected by chemical reactions, it appears that the most important variables to be considered may be listed as:

1. *Slope and spacing of liquidus and solidus lines*, which affects compositional differences between solid and liquid phases and also the duration, in time, of freezing.

2. *Diffusivity of alloying elements*, which affects degree of coring.

3. *Degree of undercooling* (changes in mold and liquid alloy temperatures, specific heats, thermal conductivities), which affects interdendritic flow of enriched liquid by its influence on: (*a*) size and shape of dendrites, or relatedly, of interdendritic channels, (*b*) relative volumes of dendrites and channels at a specific critical time during solidification, (*c*) time within critical solid-plus-liquid temperature range.

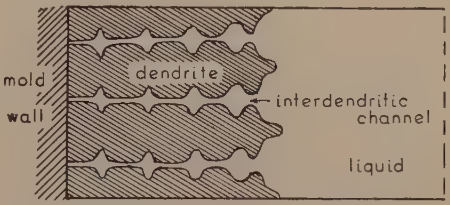

FIG. 8.—DENDRITIC CRYSTAL GROWTH FROM WALL WITH CHANNELS FILLED BY LOW-MELTING-POINT LIQUID.

Finally, it seems reasonable to believe that if no exudations occur, and if feeding is complete so that no internal cavities remain, only normal segregation could be found. However, this statement is not true, else how could inverse segregation occur in slush castings; i.e., in the solidified rim after pouring out residual liquid alloy? Since no concept advanced so far has clearly explained this phenomenon, an additional factor must be operative.

The author believes the answer is to be found in segregation in the liquid during solidification (see footnote p. 1). Coring in the solidifying dendrite has already been covered thoroughly; also, the freezing of dendrites low in solute, which causes an accompanying enrichment of the liquid in solute (Figs. 1 and 3). If we assume that the enrichment occurs only in the liquid layers immediately adjacent to the solid phase it is possible to conceive how flow of only this super-enriched liquid could cause inverse segregation in long, tapering columnar crystals (Fig. 8) and an absence of this effect in equiaxed crystals, either large (slow, uniform cooling) or fine (fast cooling with a small temperature gradient).

SUMMARY

1. Fairly rapid solidification of an alloy over a range of temperatures leads to metastable conditions of coring within solid solution dendrites and an associated abnormal enrichment in low-melting-point constituents of the final liquid to freeze.

2. The dendritic form of solidification leaves interdendritic channels, which, filled with the low-melting-point constituents, reduce the tremendous composition differences found in cored structures (microsegregation) to relatively low differences on a macro scale.

3. The formation of internal gas bubbles creates a positive pressure, forcing low-melting-point liquid to the surface, forming in extreme cases exudations; clearcut cases of inverse segregation.

4. A more fundamental consideration involves contraction and associated low-pressure areas in interdendritic channels. This present concept must be amplified by the conception of segregation in the liquid phase; i.e., an enrichment in lower-melting-point constituents at the solid-liquid interface. The flow of enriched liquid through channels may in some cases be sufficient to reverse the normal type of segregation—i.e., cause inverse segregation—but there is no clear explanation of how to control the statistical distribution of the last liquid to freeze or, relatedly, the type of segregation.

5. Three forms of gravity segregation may be found, all dependent on a marked difference in density between liquid and solid phases or between two liquid phases.

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The following references include only a few of the many papers on segregation in nonferrous alloys. The article below by Vaughn (4) should be consulted for a complete bibliography on the subject.

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DISCUSSION

(*Earle C. Smith presiding*)

THE CHAIRMAN.—We are now ready for discussion on this paper on segregation. And while Dr. Brick speaks of it as a rather elementary thing, it is the fundamental cause of many metallurgical troubles. Are there any comments?

R. S. BUSK,* Midland; Mich.—I find it quite easy to understand inverse segregation after reading this paper, since there are several very good explanations of how that may occur. But I find it very difficult to understand normal segregation in the macro sense. Dr. Brick pointed out that the coring effect is on a micro scale and cannot be detected by chemical analysis and that normal segregation is a macro effect, which is detected by chemical analysis. I wonder if he could offer an explanation as to how segregation of that type can occur in a macro sense.

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* Dow Chemical Company.

R. M. Brick.—If I understand your question correctly, Dr. Busk, you want me to explain normal segregation.

R. S. Busk.—Normal segregation must require liquid flow just as well as inverse segregation, because the coring effect is limited to the individual dendrites, which occur in multitudinous quantities on the surface of the casting.

R. M. Brick.—My reply would be that in normal segregation the mechanism of solidification is such that interdendritic flow merely carries up to the end of an interdendritic channel, that feeding is from some reservoir such as a riser, and that the casting is sound, with a central pipe or shrinkage cavity. In such a case the alloy solidifies completely first at the surface. From a straight coring effect or a statistical average of the effect, it would seem quite clear that there must be normal segregation with enrichment of the last part to freeze in low-melting-point constituents.

N. A. Ziegler,* Chicago, Ill.—The phenomenon of inverse segregation always has been of considerable interest to me. Some 15 years ago, in cooperation with Mr. O. W. Ellis, I was working on copper-tin alloys. In connection with that work, several melts of about 5 lb. weight were made in vacuum of 5 microns or better in highly refractory porcelain crucibles. Electrolytic copper and electrolytic tin were used as raw materials in proportion of 90 per cent Cu and 10 per cent Sn. When the resultant "ingots," which were solidified in vacuum, were cut very pronounced inverse segregations were discovered. In fact, the "ingots" were almost silvery in color. At that time, the phenomenon of inverse segregation was attributed to the effect of gases. Under the conditions described, however, it is difficult to see how any gas could enter into the picture.

Referring to the appearance of iron-carbon eutectic in steels, I remember having seen Ledeburite in plain carbon steels containing as low as 1.3 per cent carbon, while under equilibrium conditions eutectic should not appear unless at least 1.7 per cent carbon were present. Obviously, the Ledeburite was due to the dendritic segregation of carbon. This segregation, incidentally, was so persistent that deformed Ledeburite sometimes could be observed in forged and rolled billets containing 1.3 to 1.4 per cent carbon.

A. J. Smith,* Cincinnati, Ohio.—I believe that we are beginning this subject at the wrong end. We have some elegant theories on segregation, and we need them, in one way or another we must make the metal solid after it has been liquid, whether it goes into an ingot or a sand casting. All these theories seem to me somewhat like examining a wrecked automobile on the road and then putting a number of other automobiles through different crashes in order to find out what caused the first accident.

We do not seem to know very much about the freezing of metals. The data on actual freezing and the physics of the freezing process are very sketchy at best and I do not think anyone here could give a logical story of exactly how a metal freezes. We may theorize about normal segregation and inverse segregation, but how do these theories explain the fact that with three or four alloying constituents in a particular alloy some of the constituents will segregate normally and the others inversely? Do you assume that all the lower-melting-point metals are in a still unfrozen liquid when inverse segregation takes place? If so, all the constituents in that metal still molten should segregate inversely. But they do not behave that way.

One theory has been proposed on gas pressure, which sounds plausible—but I believe that gas must be considered one of the phases that is segregating. The gas is a perfectly good alloying constituent and will behave as an alloying constituent—so we cannot use gas as just something that carries the blame. The gas is one of the things we are segregating and we must treat it in the same way we treat the other constituents.

J. A. Rosa,† Canton, Ohio.—Dr. Brick, you say that fairly rapid solidification rate is partly responsible for the inverse segregation. I wonder if you imply that a very slow, let us say an infinitely slow, cooling rate would give a uniformly sound or uniformly homogeneous structure.

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* Crane Company.

* The Lunkenheimer Company.

† Republic Steel Corporation.

R. M. Brick.—Dr. Ziegler's interesting comments are appreciated; they supply desirable emphasis to some statements made in the paper.

The points raised by Dr. Smith are of particular interest, since so few data have been published showing segregation in ternary and more complex alloys. The fact that some elements appear to segregate normally while others segregate inversely would not at first appear to be explicable by our present theory (not theories!) of segregation. However, it is possible that the discrepancy between theory and fact is only apparent and the fault lies not with segregation theory but with knowledge of the specific ternary or quaternary phase diagram; i.e., with the probable compositions and interreactions of liquid and solid phases in the freezing range.

Mr. Rosa's hypothetical question must be answered affirmatively (if the alloy were a solid solution). Upon infinitely slow cooling, there would be no temperature gradients in the liquid. Only a few solid nuclei would form, these would be in a chemical equilibrium with the liquid at all times, diffusion within liquid and solid phases and at the solid-liquid interface would be complete and a homogeneous structure, free from segregation, would be obtained. However, it is improbable that a casting solidified under this condition would be very good; undoubtedly it would contain shrinkage cavities in addition to a coarse, soft grain structure.

E. C. Smith,* Cleveland, Ohio.—I believe the Chairman is privileged to disagree with the speaker. Clarence Tobin gave me one of these half-breed nuggets from up around Hancock, Mich., and I would say that possibly represents a grand example of slow cooling. The thing that I have never been able to figure out from all the charts, all of the phase diagrams and all of the solid solution data, is why that copper-silver nugget, which really is slowly cooled, separates itself into copper and silver? It leaves in one's mind just a little feeling of doubt that there is such a thing as a solid solution and that all we have done is to relatively rapidly cool something that wanted to separate itself into pure materials if it only had such a chance, as when mother nature takes hold of it and allows it to cool down as it ought to. And that is not the only place where you run into such occurrences. Henderson, in the Smithsonian Institution, called me to talk about the solid solution diagrams of iron and nickel in relation to nickel. I said the time schedule for meteorites does not fit the time schedule in metallurgical laboratories. I wonder, if there would not be complete segregation into complete, pure metals if we really gave them a chance to cool.

R. M. Brick.—The reply to Mr. Rosa, of no segregation on infinitely slow cooling, was based on the assumption that the alloy was a solid solution. The theory presented in this paper or in the foregoing reply is not in contradiction to the Chairman's observation on the copper-silver nugget given him by Mr. Tobin. These two elements form a eutectic system, and under extremely slow cooling conditions it is quite possible that a single eutectiferous copper-rich crystal and its accompanying silver-rich crystal could each grow in the liquid without nucleation establishing new eutectic crystals. A somewhat comparable phenomenon of relative growth and nucleation rates is observed in abnormal steels cooled extremely slowly from the annealing temperature. Here ferrite and carbide, forming from austenite, completely separate without establishing the normal eutectoid structure.

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* Republic Steel Corporation.

A Study of Age-hardening Using the Electron Microscope and Formvar Replicas

By D. Harker* and M. J. Murphy*

(New York Meeting, February 1945)

The mechanism by which age-hardening takes place is still not completely understood. The principal theories range from the extreme of "precipitation-hardening" to that of "order-hardening," with many intermediate gradations. In the hope of obtaining new data on which to base a choice among the many theories, the authors have made electron micrographs of formvar replicas taken from metallic specimens at various stages of age-hardening. The results so obtained on an alloy of 2 per cent beryllium in copper and one of 20 per cent molybdenum in iron will be described in the following pages, as well as the technique used in preparing the replicas.

Preparation of Formvar Replicas of Metallic Specimens

This section is concerned with the techniques that have proved successful in preparing formvar replicas for studying the microstructure of metals with the electron microscope. Because of its simplicity and accuracy, the formvar replica[1] method developed in the General Electric Research Laboratory has been used exclusively, since it is much simpler than the silica replica method of Heidenreich and Peck[2] and produces as good results. The formvar method to be described requires a technique acquired only by practice, and no foolproof set of rules can be given. It is a rapid method and a replica can be obtained in less than five minutes under favorable conditions. This does not mean that perfect replicas can be produced every five minutes, but rather that one can well afford to take several strippings* in order to produce a replica of high quality.

The metallographic technique required for replica work—very fine polishing and etching with very dilute solutions—is described here. It can be said, in general, that almost any surface that has been carefully prepared for a photomicrograph at 1000 or more diameters can be used to obtain a replica for the electron microscope.

Preparation of Metallographic Specimens

The preparation of the metallographic specimens is somewhat more exacting than that usually given to samples to be used for inspection under the light microscope. After much experimentation, it was concluded that the best method consists in polishing the metal through to the coarse cloth, then etching and repolishing on final cloth until the layer of distorted metal is removed. After this procedure has been completed, a dilute etch—to approximately the depth necessary for a micrograph at 1000 diameters—usually produces a sur-

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* Research Laboratory, General Electric Co., Schenectady, N. Y.

[1] References are at the end of the paper.

* Stripping is the term applied to the removal of the formvar replica from the surface of the specimen.

face suitable for production of the replica. Both a 0.25 per cent solution of nital and a 5 per cent solution of picral have been used successfully on steel specimens to be examined for pearlitic and martensitic[*] structures. Etching for a long time with dilute solution is advised, since in this way the polished surface is attacked more uniformly.

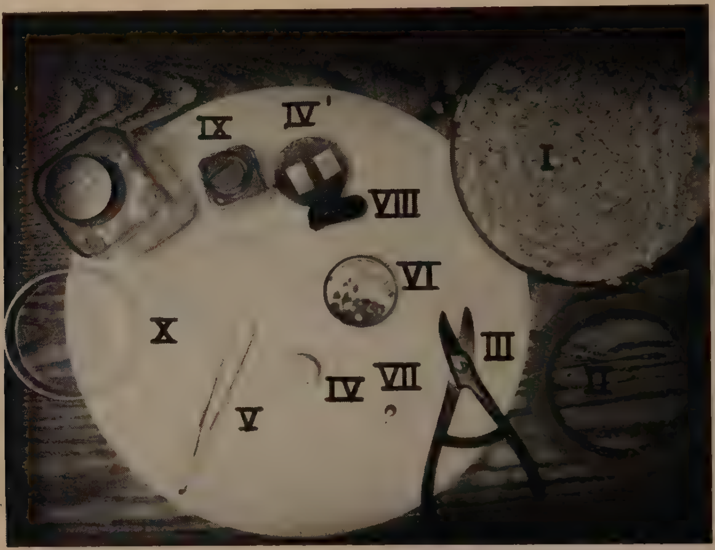

FIG. 1.—NECESSARY TOOLS.

I. Calcium chloride
II. Roll of scotch tape
III. Snippers
IV. Metallographic specimen to be stripped
IV'. Mounted specimen
V. Nonmagnetic forceps (phosphor bronze)
VI. Nickel mesh screens
VII. Specimen mount for electron microscope
VIII. Medicine dropper
IX. Solutions of formvar
X. Petri dish for use when ethylene dichloride is used as solvent

The 2 per cent beryllium in copper specimens were taken through the emery papers to the coarse cloth. After the paper scratches were removed on the coarse cloth, the specimens were deeply etched with potassium dichromate.[†] This etch was removed by the final polish. This procedure eliminated the flowed metal surface. A final swab etch with a dilute solution of one part potassium dichromate to ten parts distilled water was then given, ranging from one to five minutes, depending on the specimen. The dilute solution etched very slowly and was found to give a more representative structure than could be obtained with more concentrated solutions. The deep etching, repolishing, and light etching procedure was repeated several times until, as mentioned before, the specimens could be photographed at 1000 diameters.[*] Copper alloys have a tendency to stain, which hinders removal of the replica. Water stains on the copper were avoided by washing the sample in soap solution, removing the soap with hot water, and blowing on the surface to dry it. The results shown in Figs. 12 to 25 were all obtained from

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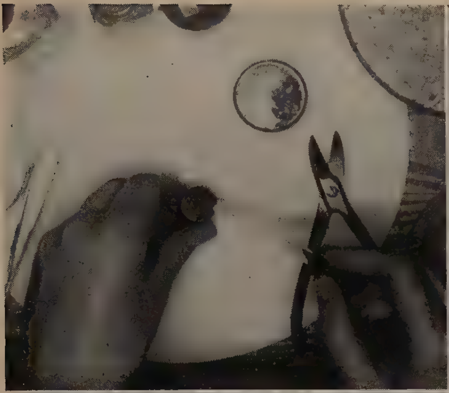
[*] Nital or a special martensite etch is probably better for martensite.

[†] 2 grams $K_2Cr_2O_7$; 8 ml. H_2SO_4; 4 ml. saturated solution NaCl; 100 ml. H_2O.

[*] It was found advisable to check the etched surface condition after each polish until the surface was considered proper for a 1000-diameter micrograph. When it was found necessary, this final etch was removed by a slight polish on the final cloth followed by repeating the dilute etch.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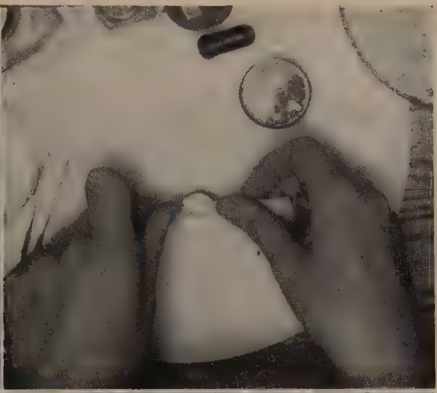
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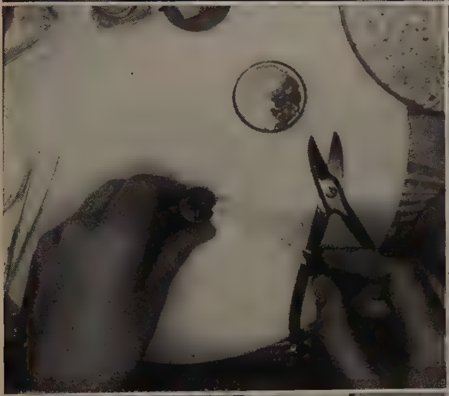
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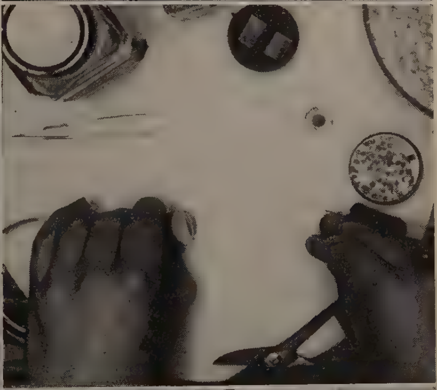
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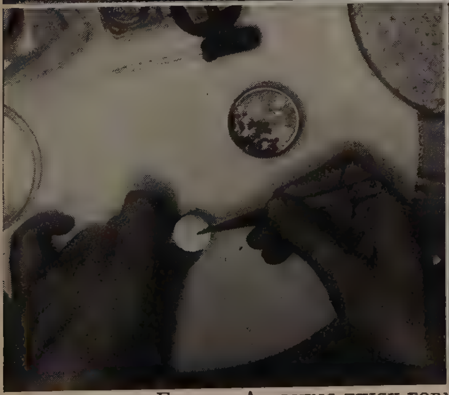
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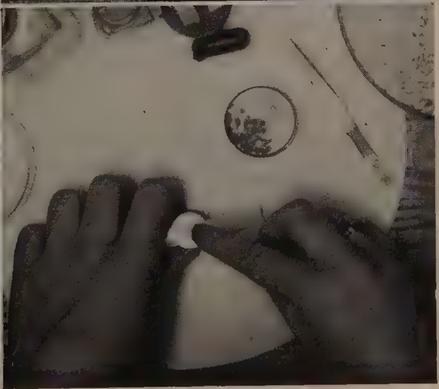
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Fig. 2.—Applying thick formvar film.
Fig. 3.—Removing thick formvar film.
Fig. 4.—Applying thin formvar film.
Fig. 5.—Draining the specimen.
Fig. 6.—Applying nickel mesh screen.
Fig. 7.—After breathing on specimen apply scotch tape

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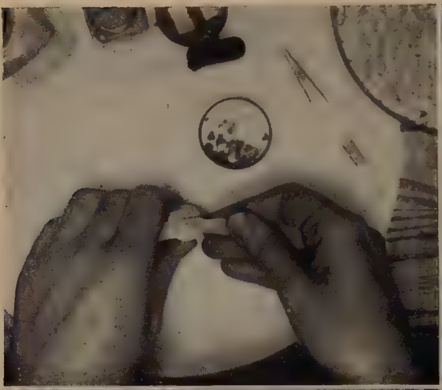

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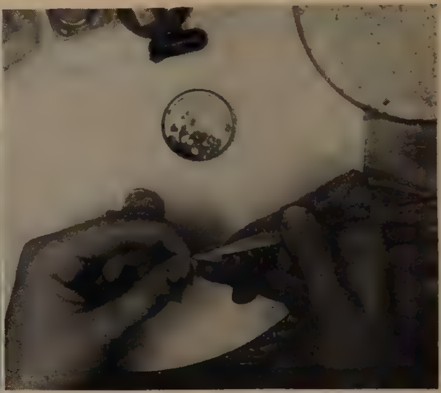

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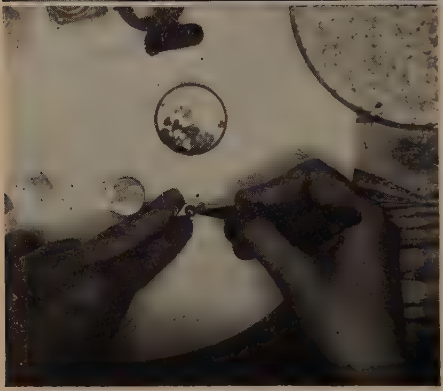


FIG. 8.—STRIPPING THIN FORMVAR FILM. Mesh now has film replica of etched surface.

FIG. 9.—REMOVING MESH FROM SCOTCH TAPE.

FIG. 10.—INSERTING MESH SUPPORTING FORMVAR REPLICA IN SPECIMEN HOLDER OF ELECTRON MICROSCOPE.

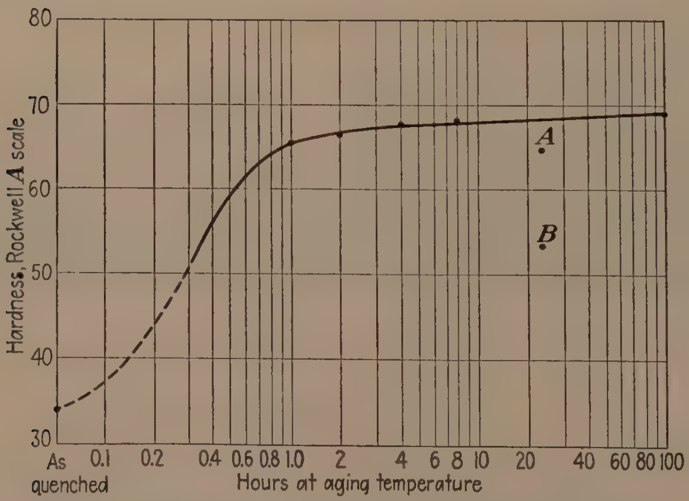
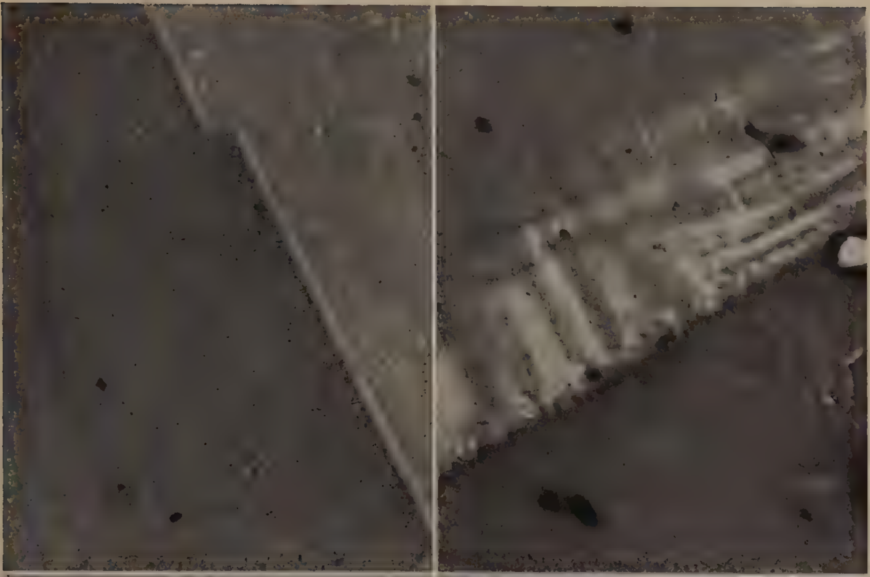


FIG. 11.—HARDNESS CURVE OF 2 PER CENT BERYLLIUM IN COPPER. Water-quenched from 850°C. Aged at 300°C. *A*, 24 hours at 400°C.; *B*, 24 hours at 500°C.



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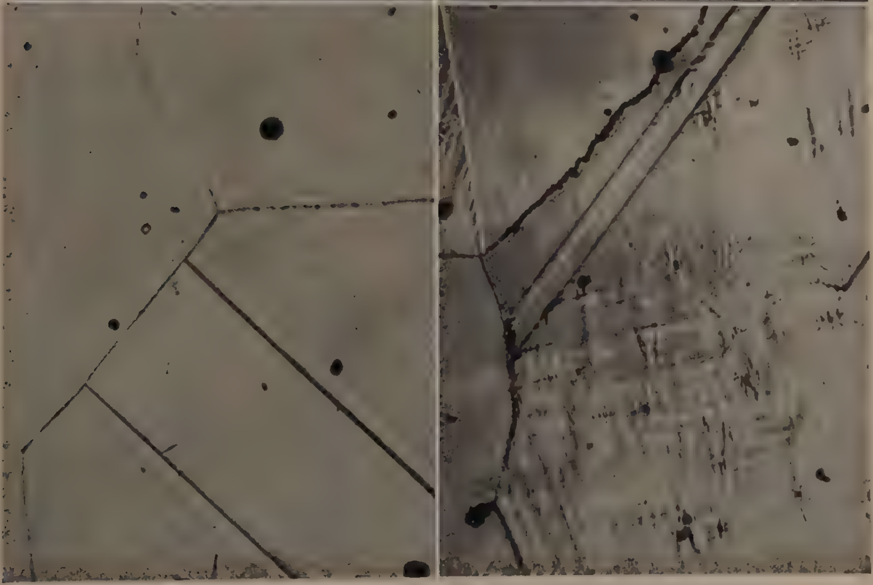

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Figs. 12 and 13.—Electron micrographs of formvar replicas of 2 per cent beryllium in copper, 2 hours at 850°C., water-quenched. × 5000.

Fig. 12, Rockwell A-33.

Fig. 13, Aged 1 hour at 300°C. Rockwell A-65.5.

Figs. 14 and 15.—Light micrographs of same specimens as in Figs. 12 and 13, respectively. × 1000.

specimens prepared by the procedure just described.

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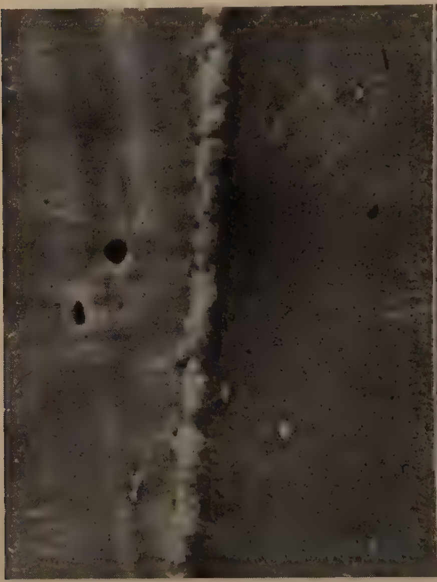

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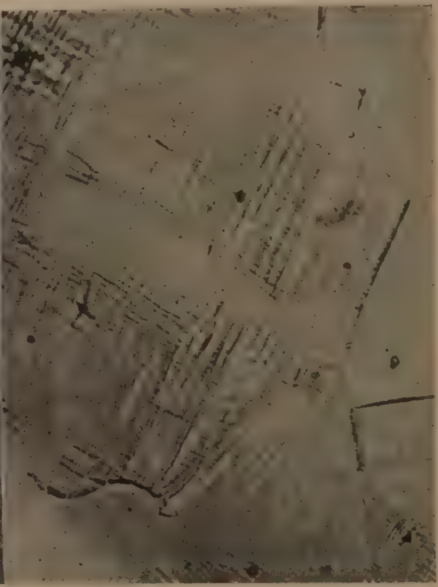


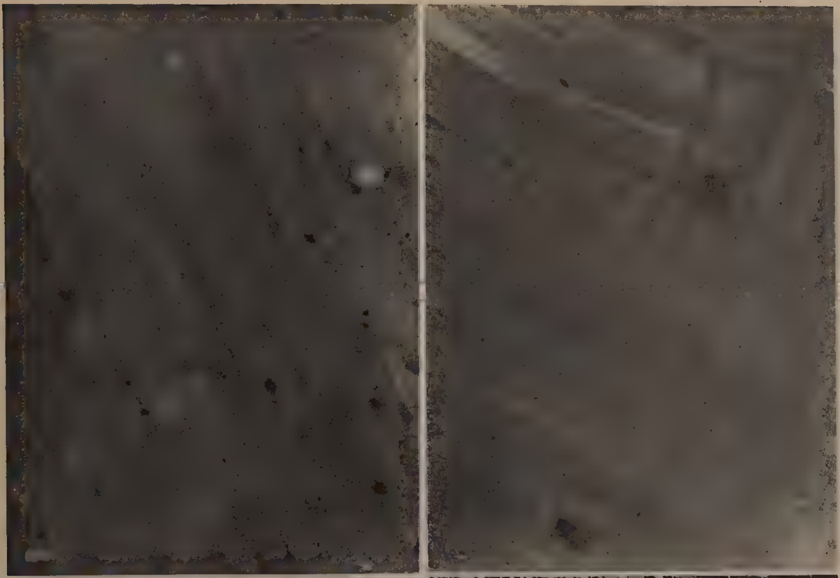
Fig. 16.—Electron micrograph of formvar replica of 2 per cent beryllium in copper, 2 hours at 850°C., water-quenched. Aged 4 hours at 300°C. Rockwell A-67.5. × 5000.
Fig. 17.—Light micrograph of same specimen as in Fig. 16. × 1000.

The 20 per cent molybdenum in iron specimens were given a careful metallographic polish and etched to a condition suitable for examination at a magnification of 1000 diameters under a light microscope. The specimens aged for 5 hr. or less were etched with the rather powerful reagent suggested by Sykes[6] (30 per cent H_2SO_4 and 5 per cent HNO_3 in water) diluted to half strength. The more thoroughly aged specimens required only the milder 0.25 per cent nital. A micrograph at a magnification of 1000 diameters was prepared from each specimen. The specimens were then used to make formvar replicas for examination in the electron microscope. The micrographs are shown in Figs. 27 to 34.

Replica Technique

Formvar replica technique[1] in the preparation of specimens for the electron microscope has now developed to the point where satisfactory results can be obtained from metallographic samples. Once the touch has been acquired, the process is relatively simple. In the General Electric Research Laboratory the work has been done primarily by the dry stripping method, using dioxane and ethylene dichloride as solvents for the formvar. Under proper conditions it is possible to obtain strippings for use with the electron microscope equally well with either solvent. (Ethylene dichloride does not give as good results as dioxane under humid weather conditions.)

Either solvent must be thoroughly dry. The moisture can be removed from ethylene dichloride by magnesium perchlorate. Since magnesium perchlorate very easily forms explosive mixtures with organic substances, proper precautions must be taken. After the drying agent has been allowed to settle out, the ethylene dichloride is filtered before the formvar is added. With dioxane, it is advisable to start with



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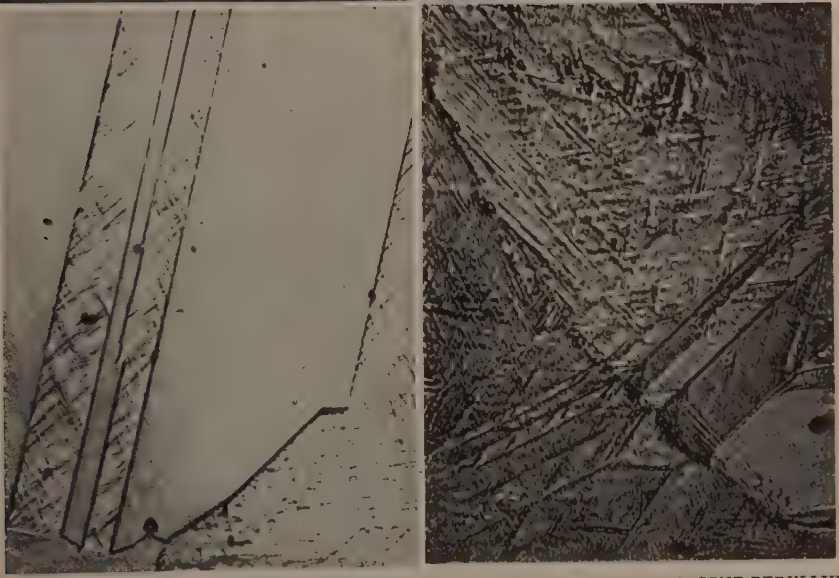

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FIGS. 18 AND 19.—ELECTRON MICROGRAPHS OF FORMVAR REPLICAS OF 2 PER CENT BERYLLIUM IN COPPER, 2 HOURS AT 850°C., WATER-QUENCHED. × 5000.

Fig. 18, aged 8 hours at 300°C. Rockwell A-68.

Fig. 19, aged 100 hours at 300°C. Rockwell A-69.

FIGS. 20 AND 21.—LIGHT MICROGRAPHS OF SAME SPECIMENS AS IN FIGS. 18 AND 19, RESPECTIVELY. × 1000.

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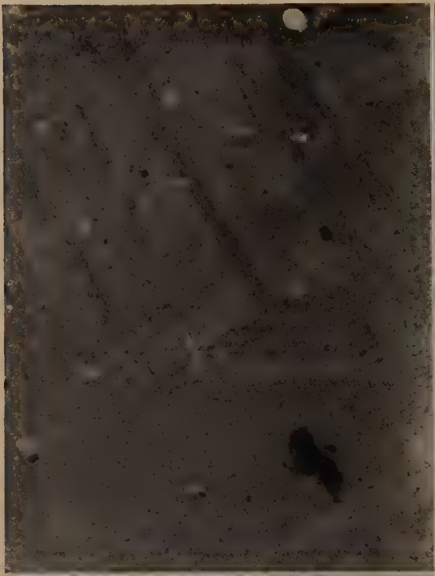

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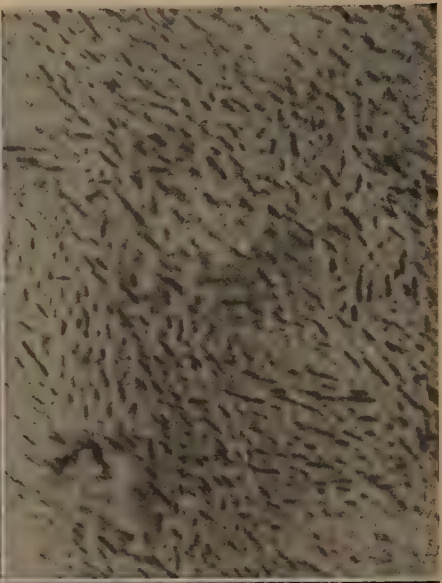

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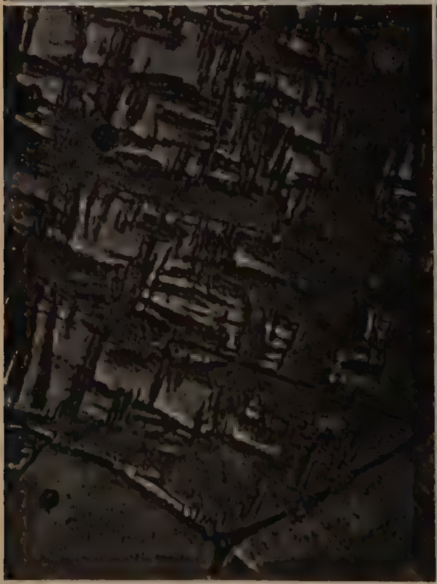

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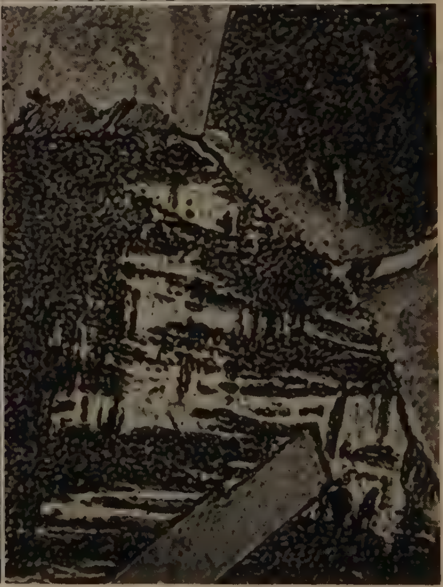

FIGS. 22 AND 23.—ELECTRON MICROGRAPHS OF FORMVAR REPLICA OF 2 PER CENT BERYLLIUM IN COPPER, 2 HOURS AT 850°C., WATER-QUENCHED. × 5000.
Fig. 22, aged 24 hours at 400°C. Rockwell A-65.
Fig. 23, aged 24 hours at 500°C. Rockwell A-53.5.

FIGS. 24 AND 25.—LIGHT MICROGRAPHS OF SAME SPECIMENS AS IN FIGS. 24 AND 25, RESPECTIVELY. × 1000.

chemically pure material, and it should be distilled over sodium before being used, in order to remove any moisture that may be present.

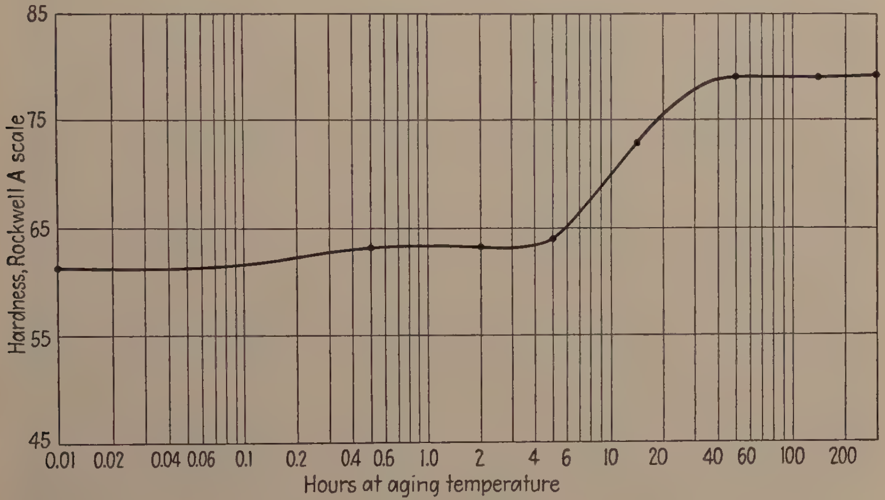

FIG. 26.—HARDNESS CURVE OF 20 PER CENT MOLYBDENUM IN IRON, WATER-QUENCHED FROM 1350°C. AGED AT 575°C.

The effectiveness of the method is increased by doing the actual stripping in an enclosed box. The box is equipped with a sealed glass top, inclined at an angle for easy vision, and two holes in the front wall for inserting the arms. A dish containing calcium chloride or sodium hydroxide, to absorb moisture, is placed inside the box. Also, the temperature is kept slightly above that of the room by lighting the interior with a 100-watt lamp. These precautions tend to give a more even film on the surface of the sample and satisfactory results have been obtained under various atmospheric conditions.

The tools used for replica work are very simple and inexpensive, as shown in Fig. 1. The replicas are made from Formvar No. 15-95, type E, dissolved in distilled dioxane or ethylene dichloride. It is convenient to have available solutions with formvar concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 per cent. The 1.0 per cent solution is used to make thick films of formvar; the others, for making replicas.

When the metallographic specimen is in proper condition to be used, it is first coated with a thick film of formvar (Fig. 2), using a concentrated solution, the removal of which cleans the surface of any harmful dirt. This film can be removed easily with scotch tape (Fig. 3): first breathe on the film a little, apply scotch tape, rub gently with the finger and remove. Usually the film will strip right off; if it does, it may be concluded that the surface is in good condition for replica work. A 0.5 per cent formvar solution, which is applied with a medicine dropper (Fig. 4), usually produces a satisfactory replica thickness for good contrast in the electron microscope. When ethylene dichloride is used as a solvent it is necessary to use a petri dish deep enough to allow the formvar solution in the specimen to be dried in the vapor of the solvent. The specimen is tilted to allow most of the solution to drain off (Fig. 5) and the solvent evaporates from the film of solution still adhering. The dried film shows interference colors, which can be used to gauge its thickness. A good uniform film shows a color that changes but slightly across the specimen. A faint yellow* indicates a proper thickness. (If the film is found to be too thick, a thinner one should be made, by using a more dilute formvar solution.) If several colors appear on the same film, this means that the film is not of uniform thickness and therefore is inferior.

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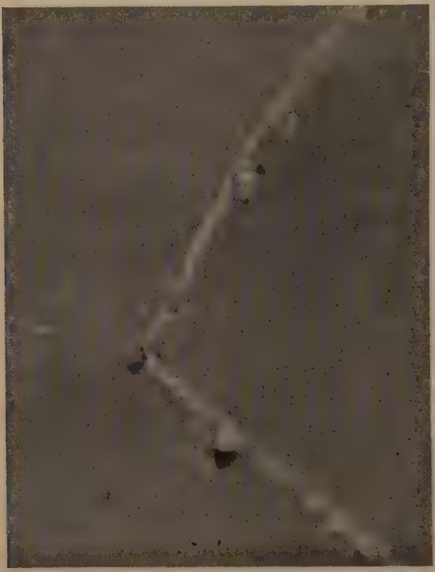

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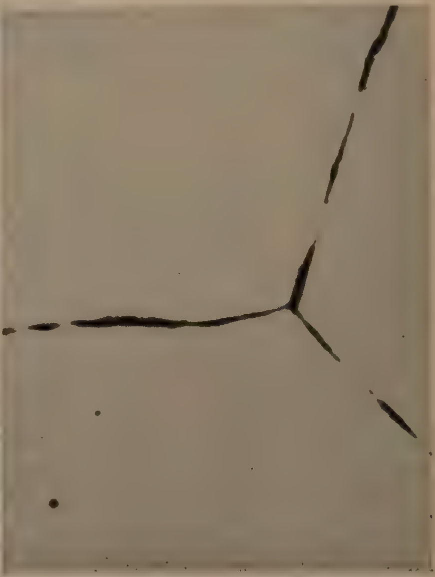

FIG. 27.—ELECTRON MICROGRAPH OF FORMVAR REPLICA OF 20 PER CENT MOLYBDENUM IN IRON, 2 HOURS AT 1350°C., WATER-QUENCHED. ROCKWELL A-61. × 10,000.

FIG. 28.—LIGHT MICROGRAPH OF SAME SPECIMEN AS IN FIG. 27. × 1000.

After the film has dried completely, the next step is to place the metal mesh—used to support the film replica in the specimen holder of the electron microscope—on the desired area (Fig. 6), which may be selected under an optical microscope if desired. The experimenter then breathes lightly on the surface in order to relax the film. Then a strip of scotch tape is applied over mesh and all (Fig. 7) and usually the film strips off easily, although sometimes a little effort is necessary. This is a part of the technique that requires some practice. The scotch tape, which covers the film, is held rigidly and one of its ends is lifted away from the specimen (Fig. 8). The mesh, which comes off with the scotch tape, is covered with a film of formvar, a stripping that is a replica of the etched surface of the metal. Often the film does not cover the entire mesh, and in such a case the nickel mesh screen may be cut to the size of the area with film on it. When areas on samples are small, it is advisable to cut the mesh before attempting to remove the replica film from the surface.

Care should be taken in removing the mesh from the scotch tape. With the tape now available, a satisfactory method is to fold the tape at the center of the mesh until the mesh adheres only at the fold, and then remove the mesh with the forceps (Fig. 9). Another method of removing the mesh with the film is to peel the scotch tape away from the mesh on a glass slide.[16] The

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* A colored metal shows its own color along with the interference color. Copper, for instance, should look deep orange-yellow under a film of proper thickness.

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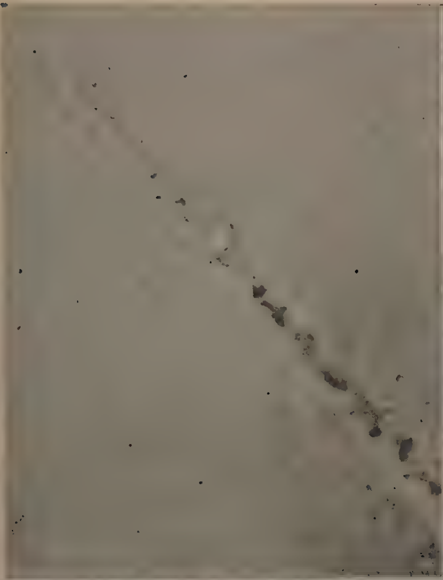

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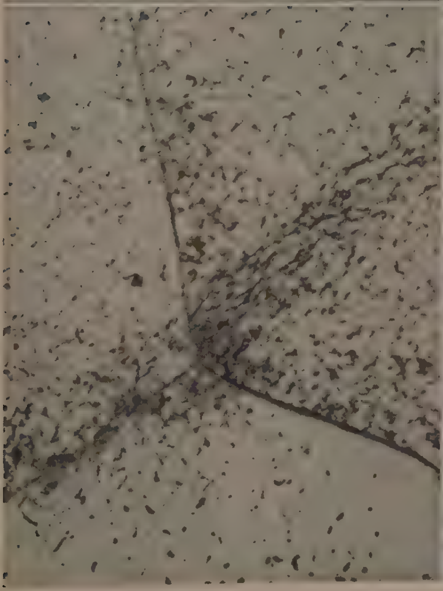

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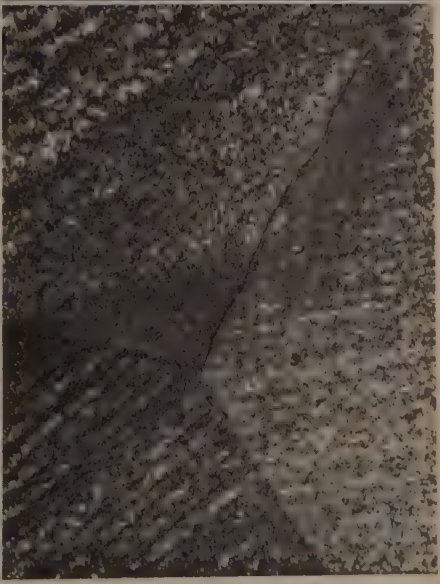

FIGS. 29 AND 30.—ELECTRON MICROGRAPHS OF FORMVAR REPLICA OF 20 PER CENT MOLYBDENUM IN IRON, 2 HOURS AT 1350°C., WATER-QUENCHED. × 10,000.
Fig. 29, aged 15 hours at 575°C. Rockwell A-73.
Fig. 30, aged 50 hours at 575°C. Rockwell A-79.
FIGS. 31 AND 32.—LIGHT MICROGRAPHS OF SAME SPECIMENS AS IN FIGS. 29 AND 30, RESPECTIVELY. × 1000.

specimen is now ready for insertion in the specimen holder of the microscope (Fig. 10). If the film is of proper thickness, around 200 to 600Å., the beam will penetrate and a pattern will appear on the fluorescent screen of the electron microscope. The best way of checking both the focus and the thickness of the film is to focus on the edge of a hole in the film. If the film is too thick for use, this edge cannot be brought into sharp focus. The etched surface can be stripped many times without injury to the specimen. After about five attempts, it is advisable to apply a thick film in order to remove any surface dirt.

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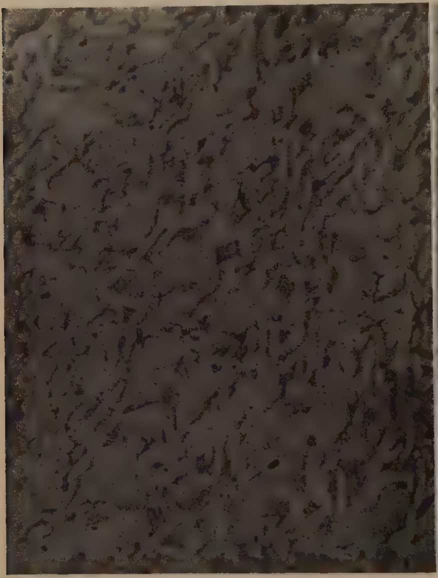

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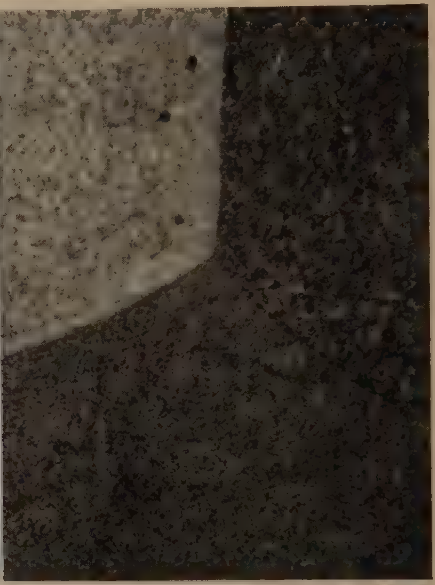

Fig. 33.—Electron micrograph of formvar replica of 20 per cent molybdenum in iron, 2 hours at 1350°C., water-quenched. Aged 306 hours at 575°C. Rockwell A-80. × 10,000.

Fig. 34.—Light micrograph of same specimen as in Fig. 33. × 1000.

After the replica has been placed in the microscope specimen holder, it is advisable to check the film under the light microscope. Using a magnification of 100 diameters, one can readily tell whether a film is present. Sometimes at 250 diameters a trace of some structure can be distinguished. This is a labor and time saver.

No practical way of examining the same area of a metallographic specimen by both the light and electron microscopes has been found. The replicas give such poor images in a light microscope that they cannot be used directly, and it is therefore necessary to examine with the electron microscope an area on a replica that corresponds to the area chosen with the light microscope on the original specimen. The 200-mesh screens on which the replicas are mounted block out about half the replica with solid metal, so that there is an even chance that the area observed under the light microscope is invisible in the electron-microscope specimen. There are also difficulties connected with reproducing positions to 0.0002 in., which have not yet been overcome. The authors expect to do more work on this problem. For the present, however, the light and electron micrographs of a specimen do not attempt to show the same area.

RESULTS FOR 2 PER CENT BERYLLIUM IN COPPER

The alloy used for this study analyzed: Cu, 97.63 per cent; Be, 2.19; Co, 0.16; Mg, 0.02. One-inch chill-cast round bars were swaged to ¾-in. diameter, cut into 1-in. lengths, and then heated for 2 hr. at 850°C. to homogenize them and dissolve any second phase that might have formed during casting. The pieces were then quenched in water. The age-hardening treatments were given to the specimens by heating them in air at various temperatures for various times and quenching in water. The treatments and hardnesses appear in Table 1 and Fig. 11.

TABLE 1.—*Heat-treatment and Hardnesses on the Rockwell A Scale of 2 Per Cent Beryllium in Copper*

(All specimens were quenched in water after two hours at 850°C., then treated as indicated and water-quenched.)

Specimen No.	Temperature, Deg. C	Time, Hr.	Hardness, Rockwell A
1		0	33
2	300	1	65.5
3	300	2	66.5
4	300	4	67.5
5	300	8	68
6	300	100	69
7	400	24	65
8	500	24	53.5

After the heat-treatment, each specimen was examined under the light microscope and used to make one or more formvar replicas for examination in the electron microscope. The results appear in Figs. 12 to 25. In the figures, the light micrograph at 1000 diameters is compared with the electron micrograph at 5000 diameters.

The constitution diagram indicates that at 850°C. the specimens of 2 per cent beryllium in copper should consist of but one phase: the cubic close-packed alpha solid solution. When the temperature is lowered to below 575°C., this phase becomes unstable and can decompose into a more dilute alpha, containing less beryllium, and gamma. The gamma phase has a crystal structure similar to that of beta brass: simple cubic, with mostly copper atoms at the cube vertices and mostly beryllium atoms at the cube centers.

Figs. 23 and 25 show that after 24 hr. at 500°C., the material is filled with a very fine precipitate, which is, no doubt, composed of gamma-phase particles. The hardness of this specimen is somewhat greater than that of the quenched one, in agreement with the idea that precipitate particles make slip more difficult. However, the photomicrographs of the specimens aged at 300°C. (Figs. 14, 15, 17, 20 and 21) show no precipitate, although their hardnesses are much greater than that of the 500°C. specimen.

The rippled appearance of the specimens aged at 300°C. seems not to be due to precipitate particles. The electron micrographs (Figures 12, 13, 16, 18, and 19) prove that the ripples are periodic changes in the resistance to etching across the specimen. A crosshatching of the ripples appears after a time and increases in amount as the aging proceeds, but this occurs only after the hardening process is essentially complete. It may be that the crosshatching marks the beginning of true precipitation. There are traces of the rippled structure in the specimen aged 24 hr. at 400°C., and there is also a well-defined precipitate in fine plates (Figs. 22 and 24). This specimen is somewhat softer than the specimens aged at 300°C.

These results accord with those of Guinier and Jacquet,[3] who observed similar ripples on aged beryllium copper. So also has Guy.[4] The ripples that appear on 25 weight per cent copper in gold alloys on aging at, say, 200°C. after quenching from above the critical ordering temperature, look very similar and suggest that the initial hardening of 2 per cent beryllium in copper is also due to ordering.[5]

RESULTS FOR 20 PER CENT MOLYBDENUM IN IRON

The alloy was made in vacuum from very pure materials and should have contained only iron and molybdenum in more than traces. Analysis for molybdenum gave 19.61 per cent of this element. The alloy was vacuum-cast into 1-in. diameter round bars, hot-swaged to ¾-in. diameter, cut to 1-in. lengths, and heated at 1350°C. for 2 hr. to ensure a homogeneous single phase. The specimens were then quenched in water. Some of the specimens were saved for standards and others were heated at 575°C. for the lengths of time shown in Table 2 and Fig. 26.

TABLE 2.—*Treatments and Hardnesses of 20 Per Cent Molybdenum in Iron*

(All specimens were heated at 1350°C. for two hours and quenched in water before the treatment shown. After the treatment, they were again water-quenched.)

Specimen No.	Temperature, Deg. C.	Time, Hr.	Hardness, Rockwell A
1		0	61
2	575	½	63
3	575	2	63
4	575	5	64
5	575	15	73
6	575	50	79
7	575	140	79
8	575	306	80

Above about 1250°C., a 20 per cent molybdenum in iron alloy consists solely of the body-centered cubic alpha phase. Below this temperature the alloy decomposes into a more dilute alpha solid solution and the epsilon phase—a compound with the formula Fe_3Mo_2. On quenching from above 1250°C., the single-phase structure is preserved in a metastable condition. To precipitate epsilon completely from the metastable alpha phase takes a long time even at relatively high temperatures such as the 575°C. used in this work.

Micrographs of the unaged specimen appear in Figs. 27 and 28. No important change in the microstructure of this alloy is visible until it has been aged more than 5 hr. at 575°C. The most that can be said is that the grain boundaries seem to thicken as time proceeds. However, after 15 hr. of aging, some precipitate has appeared, as is shown in Figs. 29 and 31. At the end of 50 hr., this precipitate has covered all the grains of the specimen. Further aging causes no apparent changes in structure.

Table 2 and Fig. 26 show that the hardnesses of the specimens correlate perfectly with their micrographs: there is no appreciable increase in the hardness until the precipitate begins to appear and no further hardening after the precipitation is complete. Here, apparently, is a case of true precipitation-hardening, for whatever process occurs during the time prior to precipitation affects neither the microstructure nor the hardness of the specimens.

SUMMARY

A method of making formvar replicas from metallic specimens, for electron-microscope work, is described in detail, as well as a procedure for preparing the specimens so that such replicas can be obtained easily.

Two age-hardening alloys are studied by both the light and electron microscopes: 2 per cent beryllium in copper and 20 per cent molybdenum in iron. The first of these shows no precipitate until after hardening is well advanced; in the other, the precipitate and hardening appear simultaneously.

ACKNOWLEDGMENTS

The authors wish to thank Mr. V. J. Schaefer for his constant interest and valuable counsel, without which it is doubtful that the formvar replica technique could have been made practical. They are also grateful to Mr. E. R. Parker, for his advice and help on the metallurgical parts of this paper; to Mrs. C. Riisness, who heat-treated the beryllium-copper

specimens; to Mr. E. T. Asp, who heat-treated the molybdenum-iron specimens; and to Mr. A. Westfall, who photographed the steps of replica preparation.

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Standards for Identifying Complex Twin Relationships in Cubic Crystals

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(New York Meeting, February 1945)

Identification of the kinds of orientation relationships that may exist among crystals is an important problem in the metallurgical field. As an aid to its solution standard orientations of several orders of twins would be very useful for rapid analyses to discover high-order as well as low-order twin relationships. Although data have been published that give orientations for three generations of twins, these data are not readily useful in the form presented; i.e., in a stereographic projection with one pole per orientation.[1] However, accurate data based on calculations of the positions of all {100} planes for such groups would be very useful when presented in tabular form. Therefore, calculations have been made for a group of four orders of twins and the data are listed in Table 3. Illustrative applications are considered briefly, with the idea of pointing out what may be done with large groups of orientations.

Method of Computing Orientation of a Twin

It is common practice to describe the orientation of a crystal in terms of the positions on a stereographic net of the poles of certain planes of the crystal. A single position on a net may be given in terms of two angle variables, two sets of which appear in the following equations:

$$\begin{array}{ll}
\textit{Polar Net} & \textit{Wulff Net} \\
x = r \sin \theta_p \cos \phi_p & x = r \cos \theta_w \\
y = r \sin \theta_p \sin \phi_p & y = r \sin \theta_w \cos \phi_w \\
z = r \cos \theta_p & z = r \sin \theta_w \sin \phi_w
\end{array}$$

The three numbers x, y and z determine a length r as well as a direction (θ, ϕ) in an X, Y, Z coordinate system. In the present case, r will be set equal to $(h^2 + k^2 + l^2)^{1/2}$, where h, k and l are the usual Miller indices for a crystallographic plane, a restriction that facilitates determination of the positions of poles of new planes from those of old or known ones,[2] as will become evident later. Furthermore, since twinned lattices have certain planes in common, it is an easy matter to determine the orientation of a twin of a crystal if the orientation of the crystal itself is known.

We start therefore with a crystal of known orientation (positions of three {100} poles given) and determine where the cube poles occur in first, second, third and fourth-order twins. Methods for identifying twinned lattices and for making the calculations to find the orientation of a twin have been published.[3,4] Reference 4 will be illustrated in the calculation of the orientation of a twin, even though this method differs from the one used by the writer in obtaining the following data on four orders of twins.

Consider a crystal S and its twin A^1, A^1 being one of the four {112} or {111} type* first-order twins of S. The orientation of S—i.e., the positions of poles of {100}

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[1] References are at the end of the paper.

planes—is given in three sets of coordinates as follows:

TABLE 1.—*Orientation of S*

Plane	Polar Net		X, Y, Z			Wulff Net	
	θ_p	ϕ_p	x	y	z	θ_w	ϕ_w
(100)	90°	45°	$\sqrt{2}/2$	$\sqrt{2}/2$	0	45°	0°
(010)	90°	135°	$-\sqrt{2}/2$	$\sqrt{2}/2$	0	135°	0°
(001)	0°	0°	0	0	1	90°	90°

According to example 1 given in reference 4, the cube poles of a (112) twin coincide in direction with the $(\bar{2}12)$, $(1\bar{2}2)$ and (442) poles of the crystal. Consequently, these latter directions in S must be found in order to locate the {100} poles of A^1.

TABLE 2.—*Orientation of A'*

Plane		Polar Net		X, Y, Z				Wulff Net	
S	A^1	θ_p	ϕ_p	x	y	z	r	θ_w	ϕ_w
$(\bar{2}12)$ or	$(\bar{3}00)$			$-3\sqrt{2}/2$	$-\sqrt{2}/2$	2	3		
$(1\bar{2}2)$ or	$(0\bar{3}0)$			$3\sqrt{2}/2$	$-\sqrt{2}/2$	2	3		
(442) or	$(00\bar{6})$			0	$4\sqrt{2}$	2	6		
	$(\bar{1}00)$	48°11′	−161°34′	$-\sqrt{2}/2$	$-\sqrt{2}/6$	$2/3$	1	135°	109°28′
	$(0\bar{1}0)$	48°11′	−18°26′	$\sqrt{2}/2$	$-\sqrt{2}/6$	$2/3$	1	45°	109°28′
	$(00\bar{1})$	70°32′	90°	0	$2\sqrt{2}/3$	$1/3$	1	90°	19°28′

First, the x, y and z values for the (200), (010) and (002) poles of S are calculated. These are then combined (as components of vectors) to obtain the x, y and z values for the $(\bar{2}12)$ pole of S (also components of a cube pole of A^1). Since r is equal to $(2^2 + 1^2 + 2^2)^{1/2}$, or 3, we now have a $(\bar{3}00)$ pole of A^1. Similar calculations can be made to obtain the x, y and z values for the $(1\bar{2}2)$ and (442) poles of S, or the $(0\bar{3}0)$ and $(00\bar{6})$ poles of A^1. These can be reduced to the x, y and z values of the $(\bar{1}00)$, $(0\bar{1}0)$ and $(00\bar{1})$ poles of A^1 by dividing each set of values by 3, 3, and 6, respectively.

Starting with the orientation of S, we therefore obtain the orientation of A^1 first in rectangular coordinates and then, with the aid of the transformation equations given earlier, in angle coordinates that can be plotted on a stereographic net. Results are as in Table 2.

In a similar way three other twins, A^2, A^3 and A^4 could be located if desired. Knowing the cube poles of A^1, three new twins $B_1{}^1$, $B_2{}^1$, and $B_3{}^1$ of A^1, or three second-order twins of S, can be found by repeating the transformations. In this way data on several orders of twins can be obtained.

Twenty-two transformations were carried through according to the letter designations shown in heavy type in Fig. 1. Data for these appear in Table 3. Angle coordinates are given to the nearest minute. However, to avoid any accumulation of error, no approximations were made in the values of x, y and z. As a result, it was possible to check all of the final values of x, y and z to see that they satisfied the following equations:

$$x_ix_j + y_iy_j + z_iz_j = 1 \text{ for } i = j \text{ and } i = 1, 2, 3$$
$$= 0 \text{ for } i \neq j$$

The first condition is met by a {100}

---

* Twinning on {112} planes or on {111} planes leads to the same four final orientations. However, {112} twins are not the same as {111} twins. Since there are only four planes of the {111} type in a crystal, there can be only one {111} composition plane per pair of {111} twins. However, {112} twins may have one, two or three composition planes per pair of twins, since a crystal has 12 planes of the {112} type.

pole; the second is met by a 90° separation of each pair of poles.

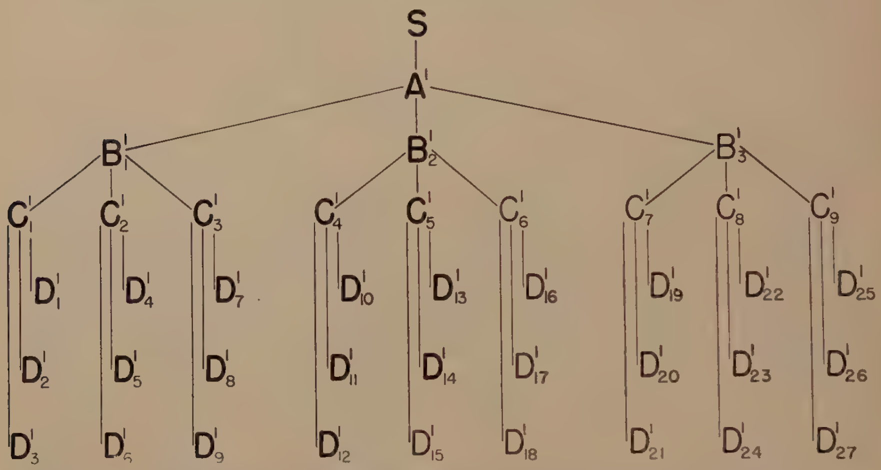

FIG. 1.—RELATIONSHIPS THROUGH FOUR ORDERS OF TWINS.
S, *A*, *B*, *C* and *D* correspond to zero, first, second, third and fourth-order twin orientations, respectively. Orientations for heavy-type letters appear in Table 3.

Coordinates of the 18 orientations shown in light type in Fig. 1 can be found readily by reflection of certain of the orientations shown in heavy type, across the *y*-axis, as follows:

$$x' = -x, \qquad y' = y, \qquad z' = z$$
$$\theta_p' = \theta_p, \qquad \phi_p' + \phi_p = \pm 180°$$
$$\theta_w' + \theta_w = 180°, \qquad \phi_w' = \phi_w$$

The relations between reflected and original orientations according to letter and subscript designations are as follows (hyphen standing for "reflection of"): B_3-B_1, C_6-C_4, C_7-C_1, C_8-C_2, C_9-C_3, D_{15}-D_{13}, D_{16}-D_{10}, D_{17}-D_{11}, D_{18}-D_{12}, D_{19}-D_1, D_{20}-D_2, D_{21}-D_3, etc. to D_{27}-D_9.

The 40 orientations shown in Fig. 1 comprise a subgroup (indicated by the superscript 1) of the 160 orientations involved in four orders of twins. The corresponding subgroups with superscripts 2, 3, and 4 can be found by increasing ϕ_p by 90°, 180°, and 270°, respectively, keeping the value of θ_p unchanged. Consequently, they can be plotted directly from the data of group 1, using either a polar net or a Wulff net.

If a standard group of orientations should be desired with *S* in a twofold symmetry position (i.e., with a (110) pole in the center of the net), it can be obtained directly from Table 3, remembering this to be a special subgroup, by means of the following transformation equations:

$$\phi_w' = \phi_w + 90°; \qquad \theta_w' = \theta_w$$

Similarly, the threefold symmetry position of *S* (a (111) pole at the center of the net) is obtained by increasing ϕ_w by 54°44′, keeping the value of θ_w unchanged.

SOME GENERAL APPLICATIONS

Special symmetry groups sometimes are very useful for analyzing data on orientations. Figs. 2 and 3 illustrate two such groups. The 13 orientations shown in Fig. 2 (orientations such as A^2, B_2^2, C_5^4 that are enclosed by dashed line circles are counted with a weight of ½) include only those of the 52 first, second, and third-order twins that have the cube pole of smallest θ_p value falling into the first quadrant; i.e., $0° \leqslant \phi_p \leqslant 90°$. Similarly,

TABLE 3.—*A Group of First, Second, Third and Fourth-order Twins (A, B, C and D, Respectively) of the Orientation S in Polar-Net, X, Y, Z, and Wulff-Net Coordinates*

Orientation	Polar Net		X, Y, Z			*Wulf Net*	
	θ_p	ϕ_p	x	y	z	θ_w	ϕ_w
S	90° 0′	45° 0′	$\sqrt{2}/2$	$\sqrt{2}/2$	0	45° 0′	0° 0′
	90° 0′	135° 0′	$-\sqrt{2}/2$	$\sqrt{2}/2$	0	135° 0′	0° 0′
	0° 0′	0° 0′	0	0	1	90° 0′	90° 0′
A^1	48°11′	−18°26′	$\sqrt{2}/2$	$-\sqrt{2}/6$	$2/3$	45° 0′	109°28′
	48°11′	−161°34′	$-\sqrt{2}/2$	$-\sqrt{2}/6$	$2/3$	135° 0′	109°28′
	70°32′	90° 0′	0	$2\sqrt{2}/3$	$1/3$	90° 0′	19°28′
B_1^1	63°37′	−105°15′	$-\sqrt{2}/6$	$-11\sqrt{2}/18$	$4/9$	103°38′	152°47′
	27°16′	59° 2′	$\sqrt{2}/6$	$5\sqrt{2}/18$	$8/9$	76°22′	66° 9′
	83°37′	161°34′	$-2\sqrt{2}/3$	$2\sqrt{2}/9$	$1/9$	160°32′	19°28′
B_2^1	63°37′	142° 8′	$\sqrt{2}/2$	$7\sqrt{2}/18$	$4/9$	135° 0′	38°57′
	63°37	37°52′	$\sqrt{2}/2$	$7\sqrt{2}/18$	$4/9$	45° 0′	38°57′
	38°57′	−90° 0′	0	$-4\sqrt{2}/9$	$7/9$	90° 0′	128°57′
C_1^1	58°46′	117°21′	$-5\sqrt{2}/18$	$29\sqrt{2}/54$	$14/27$	113° 8′	34°19′
	85°45′	−150° 4′	$-11\sqrt{2}/18$	$-19\sqrt{2}/54$	$2/27$	149°48′	171°32′
	31°35′	−53° 8′	$2\sqrt{2}/9$	$-8\sqrt{2}/27$	$23/27$	71°41′	116°12′
C_2^1	35°26′	161°34′	$-7\sqrt{2}/18$	$7\sqrt{2}/54$	$22/27$	123°22′	77°19′
	58°46′	−49°58′	$7\sqrt{2}/18$	$-25\sqrt{2}/54$	$14/27$	56°38′	141°37′
	74°58′	49°24′	$4\sqrt{2}/9$	$14\sqrt{2}/27$	$7/27$	51° 3′	19°28′
C_3^1	68°16′	21°30′	$11\sqrt{2}/18$	$13\sqrt{2}/54$	$10/27$	30°12′	47°25′
	85°45′	113°12′	$-5\sqrt{2}/18$	$35\sqrt{2}/54$	$2/27$	113° 8′	4°37′
	22°12′	−146°19′	$-2\sqrt{2}/9$	$-4\sqrt{2}/27$	$25/27$	108°19′	102°45′
C_4^1	15°39′	29° 3′	$\sqrt{2}/6$	$5\sqrt{2}/54$	$26/27$	76°22′	82°15′
	85°45′	−76°20′	$\sqrt{2}/6$	$-37\sqrt{2}/54$	$2/27$	76°22′	175°38′
	74°58′	−167°28′	$-2\sqrt{2}/3$	$-4\sqrt{2}/27$	$7/27$	160°32′	128°57′
C_5^1	68°16′	−139°34′	$-\sqrt{2}/2$	$-23\sqrt{2}/54$	$10/27$	135° 0′	148°25′
	68°16′	−40°26′	$\sqrt{2}/2$	$-23\sqrt{2}/54$	$10/27$	45° 0′	148°25′
	31°35′	90° 0′	0	$10\sqrt{2}/27$	$23/27$	90° 0′	58°25′
D_1^1	37°48′	−144°16′	$-19\sqrt{2}/54$	$-41\sqrt{2}/162$	$64/81$	119°50′	114°22′
	78°36′	−39°13′	$29\sqrt{2}/54$	$-71\sqrt{2}/162$	$16/81$	40°35′	162°19′
	54°32′	59° 2′	$8\sqrt{2}/27$	$40\sqrt{2}/81$	$47/81$	65°14′	39°43′
D_2^1	46°16′	25° 1′	$25\sqrt{2}/54$	$35\sqrt{2}/162$	$56/81$	49° 6′	66° 9′
	75°42′	−79° 6′	$7\sqrt{2}/54$	$-109\sqrt{2}/162$	$20/81$	79°26′	165°27′
	47°14′	177°16′	$-14\sqrt{2}/27$	$2\sqrt{2}/81$	$55/81$	137°10′	87° 3′
D_3^1	69°47′	−12°21′	$35\sqrt{2}/54$	$-23\sqrt{2}/162$	$28/81$	23°34′	120° 9′
	20°14′	169°49′	$-13\sqrt{2}/54$	$7\sqrt{2}/162$	$76/81$	109°54′	86°16′
	89°18′	77°54′	$4\sqrt{2}/27$	$56\sqrt{2}/81$	$1/81$	77°54′	0°43′
D_4^1	75°42′	−0°31′	$37\sqrt{2}/54$	$-\sqrt{2}/162$	$20/81$	14°18′	92° 1′
	57° 6′	98°58′	$-5\sqrt{2}/54$	$95\sqrt{2}/162$	$44/81$	97°31′	33°13′
	36°38′	−110°33′	$-4\sqrt{2}/27$	$-32\sqrt{2}/81$	$65/81$	102° 6′	124°51′
D_5^1	37°48′	10°40′	$23\sqrt{2}/54$	$13\sqrt{2}/162$	$64/81$	52°58′	81°50′
	57° 6′	−135°51′	$-23\sqrt{2}/54$	$-67\sqrt{2}/162$	$44/81$	127° 2′	137° 7′
	73°30′	123° 7′	$-10\sqrt{2}/27$	$46\sqrt{2}/81$	$23/81$	121°35′	19°28′
D_6^1	84°20′	97°34′	$-5\sqrt{2}/54$	$113\sqrt{2}/162$	$8/81$	97°31′	5°43′
	78°36′	−171°18′	$-37\sqrt{2}/54$	$-17\sqrt{2}/162$	$16/81$	165°42′	126°55′
	12°46′	−18°26′	$4\sqrt{2}/27$	$-4\sqrt{2}/81$	$79/81$	77°54′	94° 6′
D_7^1	46°16′	−61°53′	$13\sqrt{2}/54$	$-73\sqrt{2}/162$	$56/81$	70° 6′	132°40′
	66°44′	−176°11′	$-35\sqrt{2}/54$	$-7\sqrt{2}/162$	$32/81$	156°26′	98°48′
	52°47′	74°45′	$4\sqrt{2}/27$	$44\sqrt{2}/81$	$49/81$	77°54′	38°13′
D_8^1	37°48′	107°24′	$-7\sqrt{2}/54$	$67\sqrt{2}/162$	$64/81$	100°34′	53°29′
	69°47′	−134°15′	$-25\sqrt{2}/54$	$-77\sqrt{2}/162$	$28/81$	130°54°	152°47′
	59°35′	−31°46′	$14\sqrt{2}/27$	$-26\sqrt{2}/81$	$41/81$	42°50′	131°53′
D_9^1	57° 6′	154°46′	$-29\sqrt{2}/54$	$41\sqrt{2}/162$	$44/81$	139°25′	56°37′
	32°55′	−23°41′	$19\sqrt{2}/54$	$-25\sqrt{2}/162$	$68/81$	60°10′	104°34′
	89°18′	−114°47′	$-8\sqrt{2}/27$	$-52\sqrt{2}/81$	$1/81$	114°46′	179°13′

TABLE 3.—(*Continued*)

Orientation	Polar Net		X, Y, Z			Wulff Net	
	θ_p	ϕ_p	x	y	z	θ_w	ϕ_w
D_{10}^1	57° 6′	−117°54′	$-5\sqrt{2}/18$	$-85\sqrt{2}/162$	$44/81$	113° 8′	143°48′
	60°24′	−6°20′	$11\sqrt{2}/18$	$-11\sqrt{2}/162$	$40/81$	30°12′	101° 0′
	47°14′	115°21′	$-2\sqrt{2}/9$	$38\sqrt{2}/81$	$55/81$	108°19′	45°40′
D_{11}^1	84°20′	56°27′	$7\sqrt{2}/18$	$95\sqrt{2}/162$	$8/81$	56°38′	6°47′
	37°48′	153°48′	$-7\sqrt{2}/18$	$31\sqrt{2}/162$	$64/81$	123°22′	71° 6′
	52°47′	−37°52′	$4\sqrt{2}/9$	$-28\sqrt{2}/81$	$49/81$	51° 3′	128°57′
D_{12}^1	78°36′	−28°10′	$11\sqrt{2}/18$	$-53\sqrt{2}/162$	$16/81$	30°12′	156°53′
	32°55′	−136°18′	$-5\sqrt{2}/18$	$-43\sqrt{2}/162$	$68/81$	113° 8′	114° 5′
	59°35′	68°38′	$2\sqrt{2}/9$	$46\sqrt{2}/81$	$41/81$	71°41′	32°13′
D_{13}^1	78°36′	103°55′	$-\sqrt{2}/62$	$109\sqrt{2}/162$	$16/81$	103°38′	11°44′
	20°14′	−132°57′	$-\sqrt{2}/6$	$-29\sqrt{2}/162$	$76/81$	103°38′	105° 6′
	73°30′	10°29′	$2\sqrt{2}/3$	$10\sqrt{2}/81$	$23/81$	19°28′	58°25′
D_{14}^1	46°16′	11°51′	$\sqrt{2}/2$	$17\sqrt{2}/162$	$56/81$	45° 0′	77°53′
	46°16′	168° 9′	$-\sqrt{2}/2$	$17\sqrt{2}/162$	$56/81$	135° 0′	77°53′
	77°53′	−90° 0′	0	$-56\sqrt{2}/81$	$17/81$	90° 0′	167°53′

Fig. 3 illustrates a group of fourth-order twins (one fourth of 108 orientations), the letter *D* being omitted and the superscript dropped except for D_{14}^1 and D_{14}^4. It is clear that θ_p, in the first quadrant, is restricted to a maximum value of 54°44′ if any orientation is plotted in this manner, the 54°44′ occurring when θ_p for a $\{111\}$ pole of a crystal is equal to zero.

To illustrate the use of these plots, suppose two orientations, *E* and *F*, are being compared, *E* in the position of *S* and *F* in its proper relative position. If *F* is one of the 52 first, second, and third-order twins, it will also be one of the orientations shown in Fig. 2, provided *E* is rotated into the proper one of the four equivalent positions of *S*. We can go even further than this. For example, if *E* is put into the position of *S* in such a way that the cube pole of *F* that is nearest to any cube pole of *E* (and this one must be brought to the center of the net) lies not only in the first quadrant but also in the range $0° \leqslant \phi_p \leqslant 45°$, then *F* must check with one of the following: A^3, B_3^4, C_3^3, or C_4^1. In like manner, agreement with one of the fourth-order twins produces a check with one of the following five: D_{24}, D_{15}, D_{21}, D_{22}, and D_7.

In using these general classes we need to know the members as well as the size of each class; therefore these are grouped together as follows in the order of first, the general class (designated by a starred letter), second, the members, and, finally, the size or relative weight (allowance being made for some members having a weight of ½): A^*, A^3, A^2, 1; B^*, B_2^3, B_1^1, B_3^4, B_2^2, 3; C_3^*, C_3^3, C_9^2, C_5^1, C_5^4, 3; C_4^*, C_4^1, C_6^4, C_1^2, C_7^3, C_8^1, C_2^4, 6; D_7^*, D_7, D_{25}, D_{14}^1, D_{14}^4, 3; D_{15}^*, D_{15}, D_8, D_9, D_{13}, D_{26}, D_{27}, 6; D_{21}^*, D_{21}, D_3, D_5, D_{12}, D_{18}, D_{23}, 6; D_{22}^*, D_{22}, D_2, D_4, D_{10}, D_{16}, D_{20}, 6; and D_{24}^*, D_{24}, D_1, D_6, D_{11}, D_{17}, D_{19}, 6.

A study of Fig. 1 would lead one to expect some such reduction to nine classes. However, since rotations can be made easily with the aid of a Wulff net, the groupings listed above were determined by the graphical method. Another point of interest is the fact that *S* can be brought into the position of A^*, B^*, C_3^* or D_7^* by one axis of rotation ($<110>$ type), whereas two axes are required for the remaining five classes. Fig. 4 is a plot of the nine general classes.

We may be interested in cases where an orientation group, for example, *E* and *F*, does not fit exactly or even within the range of experimental error into this system of twin orientations. Methods for dealing with such cases have been developed, which allow for inexact variations in orientations.[5] For example, results may be evaluated by means of probability methods applied to an orientation state rather than to a single orientation.

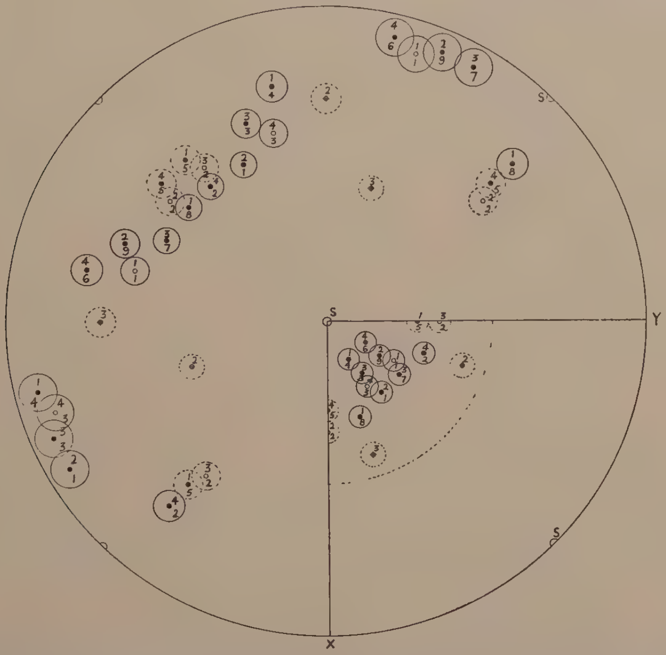

FIG. 2.—STEREOGRAPHIC PLOT OF GROUP OF THIRTEEN ORIENTATIONS FROM FIRST THREE ORDERS OF TWINS.

Large open circles indicate weight of ½. Small white circle indicates second order; small black circle, third order; circle with cross, first order. α is 3°41′. Positions of cube poles are given.

A state is determined as follows: Consider all {100} poles of an orientation A located on a stereographic net to be enclosed by small circles of radius α. If the cube poles of an orientation B fall within these circles, B is said to be in the state A; i.e., it agrees with the orientation A to within the specified range of α radians. If we should speak of the 52 first, second, and third-order twins as 52 states, we might ask, "How large can α become before the 52 stages are not any longer unique?" The answer is 3°41′, the size of a state illustrated in Figs. 2 and 3. It will be noted that circles for the group shown in Fig. 2 begin to overlap for α equal to 2°36′, however, degeneracy among the states does not occur at this point. Although there are 108 fourth-order twins, there is no degeneracy among such states for α equal to 3°41′ (Fig. 3). In practical applications various values of α may be used and the evaluation of results made in terms of probabilities.

To illustrate, we would like to know the probability P that a nucleation during recrystallization would produce an orientation by chance alone that would agree with one of the states in the system of twins described. It has been shown[5] that the probability $P(E)$ that a single nucleation will produce an orientation B that falls into a state E (i.e., within α radians of an orientation A as described) is:

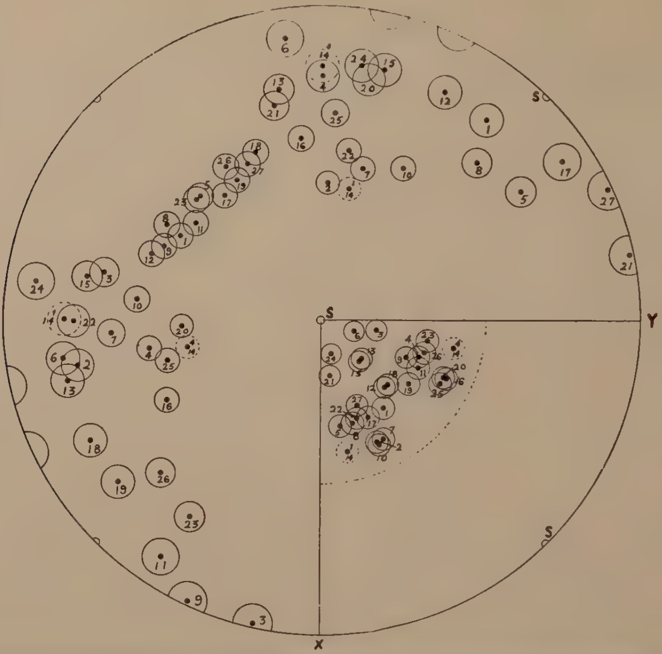

FIG. 3.—STEREOGRAPHIC PLOT OF TWENTY-SEVEN FOURTH-ORDER ORIENTATIONS. α IS $3°41'$.

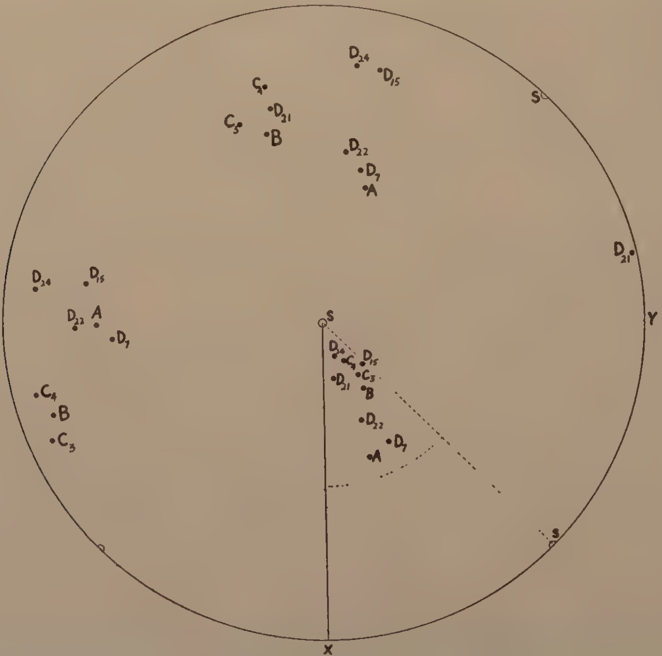

FIG. 4.—STEREOGRAPHIC PLOT OF NINE GENERAL CLASSES, INCLUDING FIRST, SECOND, THIRD, AND FOURTH-ORDER TWIN ORIENTATIONS.

$P(E) = 1.43\alpha^3$. If we set this equal to $1/N$, we may think of N as being the maximum number of states into which B might have fallen. For the special case already discussed, where α is just equal to $3°41'$, N equals 2630 states. Suppose we limit the number of twin states to 52, so as to include the first, second, and third-order twins. The probability P that B, relative to the parent grain, will be one of these 52 orientations is: $P = {}^{52}/_{2630}$ or $1/50.6$. Again, if α is made equal to $5°$, the probability P still has a significant value, even though there is some degeneracy among the 52 states. The value for P in this case is about ${}^1/_{22}$.

Although there may be many ways in which the methods described could be applied, suppose, as a final illustration, a case where an old grain recrystallized into many new grains by means of a mechanism involving near, but not exact, second-order twins. Further, suppose the orientation of the old grain had not been obtained. Analyses for relationships among the new grains by the foregoing methods would show at most a general agreement for second-order and fourth-order twins—a result very suggestive of a second-order twin relationship with the old grain. If groups of nearly common orientation were also encountered individual orientations probably could be replaced by average orientations or orientation states. However, if all nuclei should fall into one state to produce a single preferred crystal orientation, no analysis could be made without having the orientation of the old grain.

Finally, it may be pointed out that some of the foregoing methods have been used in the analysis of recrystallization data for silicon ferrite.[6]

ACKNOWLEDGMENT

It is a pleasure to acknowledge the aid of Miss Blanche Eulian in constructing diagrams and checking data and of Miss Jean McAllister in carrying through the calculations on four orders of twins.

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Orientation Changes during Recrystallization in Silicon Ferrite

By C. G. Dunn,* Member A.I.M.E.

(New York Meeting, February 1945)

With respect to theories of recrystallization in metals plastically deformed, it has been said that the present status of this subject is far from satisfactory.[1] It may also be said that before any mechanism of recrystallization for metals and alloys can be set forth in a satisfactory manner, there must be made available considerable data on orientation changes that occur during the deformation and recrystallization processes. Although extensive data have been published on recrystallization in single crystals and in polycrystalline specimens, more results of a type that can be classified according to simple orientation changes would be desirable in this complex field.

It might even be said that before classifications are made according to types of orientation changes, it may be possible to classify a considerable amount of data into certain kinds of orientation states if groups of common or nearly common orientation occur. Methods for computing the probability of occurrence for various types of groups have been published[2] and it has been pointed out in particular that it should be possible to analyze orientation data for high-order twin relationships between old and new grains even when agreement is not at all exact. In this connection, work on recrystallization in silicon ferrite reported in a paper concerned with complex groups of annealing twins[3] indicated that some data were consistent with primary nucleation occurring according to a second-order or a third-order twin transformation. However, further work in this latter direction was definitely needed.

It is, therefore, the purpose of the present paper to report data and analyses for primary nucleation in silicon ferrite following small deformations that have been carried out at the Pittsfield Works' Laboratory of the General Electric Co. Analyses have been made with the aid of standard groups of twins that are reported elsewhere.[4]

Preparation of Specimens and Experimental Procedure

The material used in the present investigation was taken from the same heat of steel as that used in a prior report.[3] The finished strip in both cases was made by the Allegheny-Ludlum Steel Corporation according to methods that produce a high degree of preferred crystal orientation. Samples with large grains had the following composition: 3.45 per cent Si, 0.003 C, 0.008 P, 0.020 S, 0.075 Mn, 0.031 Al and 0.072 Cu. Thickness of specimens was 0.012 inches.

Plastic deformation was produced by cold-rolling the samples on a mill with 8-in. diameter rolls, the plane of the sample in each case coinciding with an XY plane (the plane of projection for the stereographic plots) and the elongation occurring in the X direction. In general, elongations were held to about 3 or 4 per cent.

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[1] References are at the end of the paper.

Various kinds of anneals were tried in an endeavor to obtain early stages of recrystallization and thus have old and new orientations together at the same time. This was done to overcome two kinds of difficulty encountered in this low reduction range; namely, the samples either recrystallized in such a way that the origin of recrystallization nuclei could not be established, or they failed to recrystallize. In either case early X-ray work if carried out was essentially wasted. However, complete data could be obtained in a relatively simple way following the anneal. For example, after the cold-rolling operation, both surfaces S_1 and S_2 of a specimen were etched lightly to bring out the original grain boundaries and also Neumann bands, if these were produced by the deformation. S_1 and S_2 were essentially mirror images of each other, the grains being as thick as the specimens. Since these surfaces could be retained during an anneal in an atmosphere of pure, dry hydrogen, it was not necessary to photograph specimens prior to the anneal. Incidentally, it was found possible to register the original orientation of grains that were completely recrystallized in the anneal, provided annealing was held to a maximum temperature of about 900°C., one surface—say S_1 in this case—receiving an etch-pit treatment prior to the anneal. In general, no evidence of recrystallization could be seen immediately following the first anneal. However, a relatively light etch applied to surface S_2 would suffice to show any recrystallization, and this could be done without destroying the record carried on surface S_1.

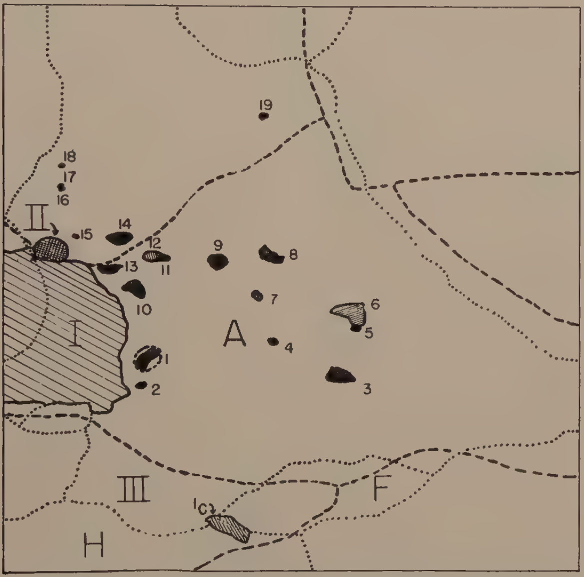

FIG. 1.—PART OF SPECIMEN D32, SHOWING ORIGINAL GRAINS (DOTTED LINES), NEW GRAINS AFTER THE FIRST ANNEAL (SHADED AREAS), AND FINAL GRAINS AFTER A SECOND ANNEAL (HEAVY BROKEN LINES). × 3.75.

A large number of samples were cold-rolled, annealed, and treated in this way to get specimens that would be suitable for the present investigation.

Cold-rolling and annealing schedules are given in Table 1 for four samples that were investigated in detail.

Sample D2 was one of a group given a single surface etch-pit treatment prior to the anneal.

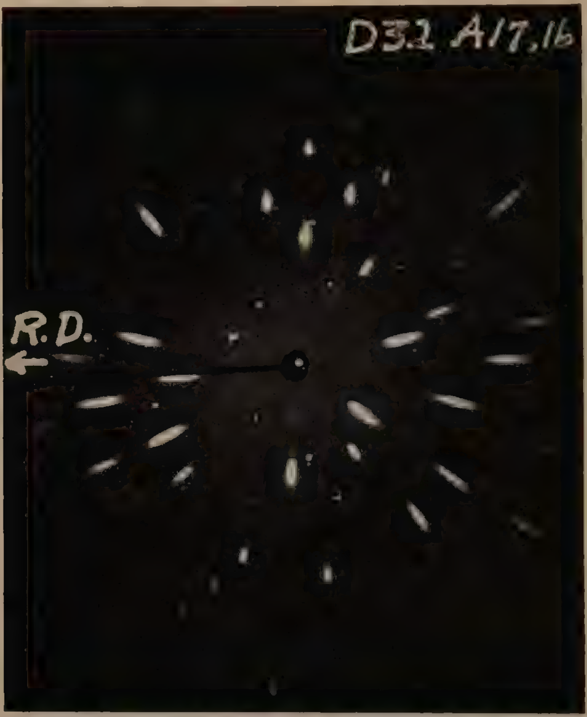

FIG. 2.—LAUE DIFFRACTION PATTERN OF GRAIN *A* IN SPECIMEN D32, TOGETHER WITH TWO NEW GRAINS, 16 AND 17.

Specimens D1 and D32 proved to be valuable for studying two stages of recrystallization because the first anneal produced partial recrystallization in isolated areas and the second anneal completed the recrystallization process.

TABLE 1.—*Cold-rolling and Annealing*

Specimen	Percentage of Reduction	First Anneal	Second Anneal
D32	3	500°–800°C. in 15 hr.	800°–1000°C. held 2½ hr.
D53	4	½ hr. at 1000°C.	None
D1	4	500°–800°C. in 15 hr.	800°–1000°C. held 2½ hr.
D2	4	500°–800°C. in 15 hr.	None

Transmission Laue diffraction patterns were obtained on new and old grains to determine grain orientations. The method used here was the same as that employed previously.[3]

EXPERIMENTAL RESULTS

A number of recrystallization nuclei were found in specimen D32 after the first anneal. In the region of grain *A* of this specimen, the nuclei were distributed as shown schematically in Fig. 1. These nuclei, or new grains, designated by numbers, are the shaded areas in the figure. Original grain boundaries are shown by dotted lines and old grains are marked by letter. Grain boundaries for the same

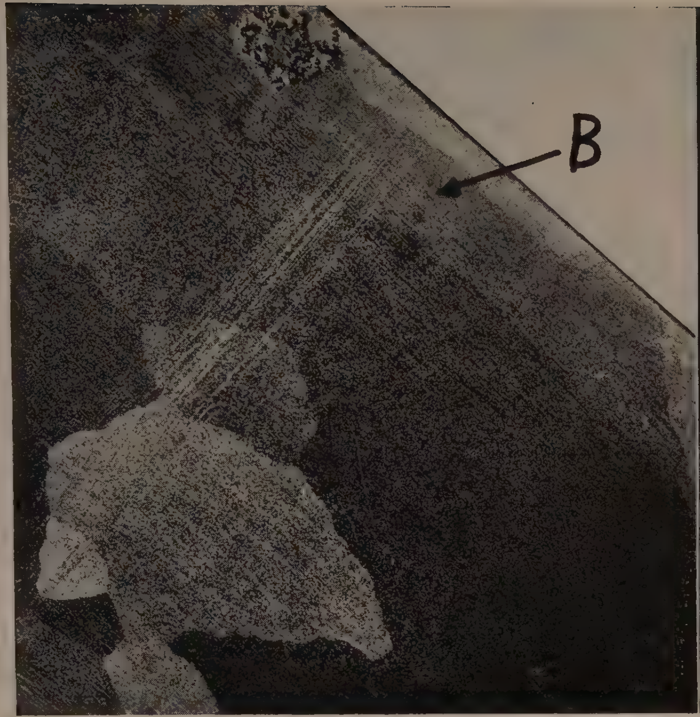

FIG. 3.—RELIEF MAP OF ORIGINAL GRAINS AND NEUMANN BANDS OF PART OF SPECIMEN D_2 RETAINED IN AN 800°C. DRY-HYDROGEN ANNEAL. × 3.

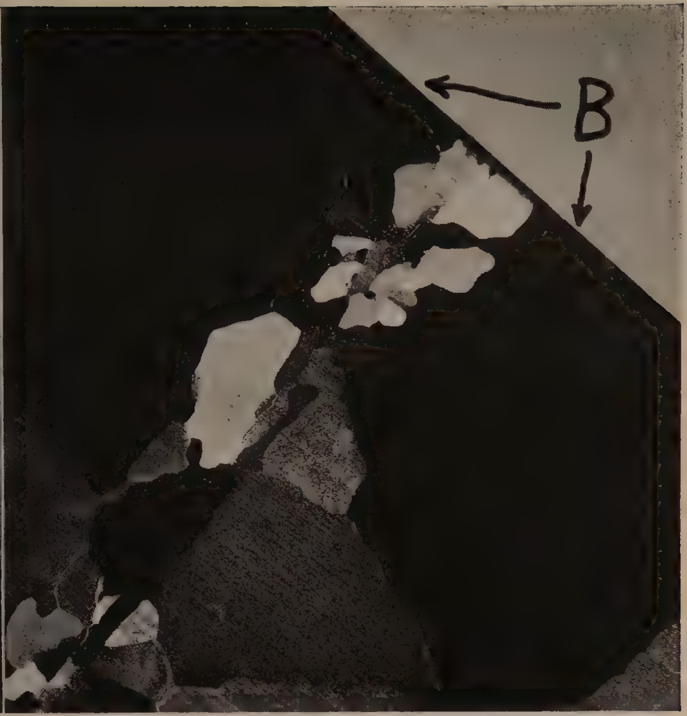

FIG. 4.—SAME AREA AND SURFACE SHOWN IN FIG. 3 AFTER ETCHING WITH NITRIC ACID TO UNCOVER NEW STRUCTURE. × 3.

region of D32 following the second anneal are shown by the heavy dashed lines. There were 19 nuclei within grain *A*. At the common boundaries of old grains *A*, *H* and *F* there was a nucleation 1_e. Fig. 2 is an illustrative Laue diffraction pattern of nuclei 16 and 17, together with old grain *A*. All 19 nuclei within grain *A* except No. 1 disappeared during this second anneal. Nucleus No. 1 grew a small amount but grain I shown at the left grew into the area on the right and removed nuclei 2, 10, 13, etc.; grain II grew and removed nuclei 14, 15, etc., and grain 1_e grew at the expense of *A*, *H* and *F* to become grain III.

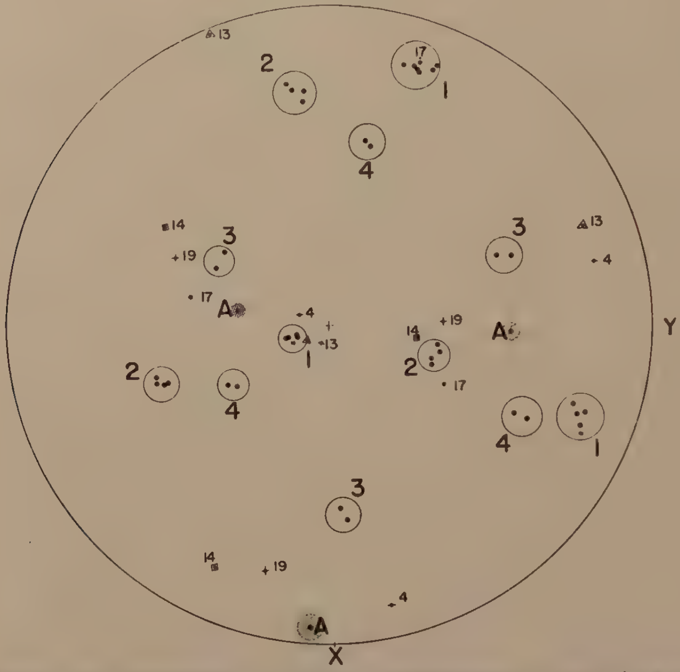

FIG. 5.—STEREOGRAPHIC PROJECTION OF ORIGINAL ORIENTATIONS OF GRAIN *A* OF SPECIMEN D32 AND ITS 19 RECRYSTALLIZATION NUCLEI.

Cube poles of *A* are enclosed by circles of 5° radius. Groups of common orientation are indicated by states 1, 2, 3 and 4.

Complete recrystallization occurred in the central region of grain *A* of specimen D53 to form a group of 10 grains that ranged in size from 0.4 to 10 mm. The average diameter of grain *A* was about 20 millimeters.

One grain-boundary nucleation D1 — 1_e occurred in specimen D1 at the boundary of grains *A* and *B*. It was a very tiny grain, not as thick as the specimen; so a single X-ray diffraction pattern sufficed to register it and grains *A* and *B*. In the second anneal, which completely recrystallized the specimen, *D*1 — 1_e grew not only into a very large grain but also one containing island twin orientations of a type previously described.[3] In this case the large or primary grain contained only two types of twins, presumably developed in the anneal by a dependent nucleation process.

Upon etching one surface (S_2) of specimen D_2 after the 800°C. anneal, it was found that recrystallization had occurred among the Neumann bands. Photographs of surface S_1 after this anneal and then again after etching with dilute nitric acid to remove the relief map of the original origins are shown in Figs. 3 and 4, respectively. Thirty-three new grains within the old boundaries of grain *B* were X-rayed along with the residue of grain *B*. Orientations of all the grains, new and old, that were obtained for the four specimens are given in Tables 2 to 5 under the column headed "Original Orientations." These orientations are accurate to within about one degree. Figs. 5 and 6 are stereographic projection plots for D32*A* and D2*B*, respectively, the general amount of spread in orientation of old grains *A* and *B* being given by the size of shaded areas.

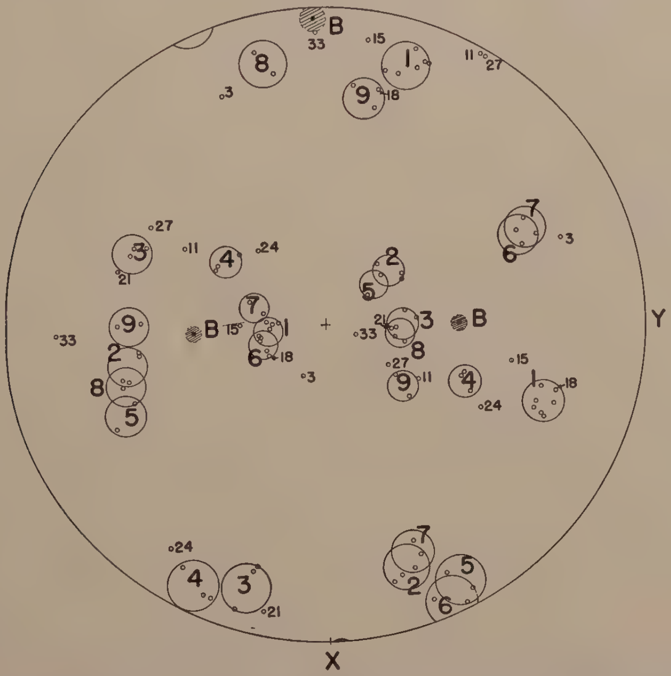

FIG. 6.—STEREOGRAPHIC PROJECTION OF ORIGINAL ORIENTATIONS OF GRAIN *B* OF SPECIMEN D2 AND ITS 33 RECRYSTALLIZATION GRAINS.

Cube poles of *B* are enclosed by circles of 5° radius.

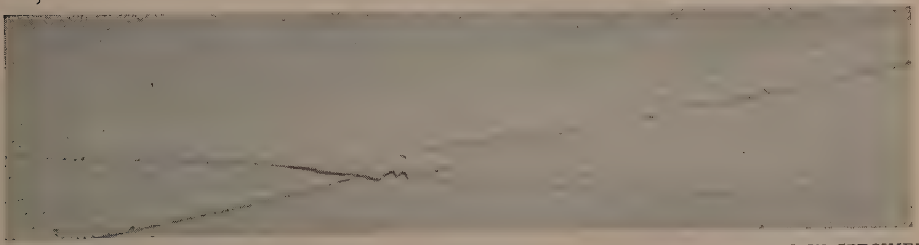

FIG. 7.—APPEARANCE OF NEUMANN BAND AT INTERSECTION POINT OF TWO BANDS IN SPECIMEN COLD-ROLLED 4 PER CENT. × 1000.

It would not be possible to show a representative microstructure of the cold-rolled samples as far as Neumann bands are concerned, but Fig. 7 has been included

TABLE 2.—*Recrystallization Data for Grain A in Specimen* D32, *Together with Analyses Made Using High-order Twin Groups*

Angles are given in degrees and positions of {100} poles are given in polar net coordinates

Grain		Original Orientation		Rotated Group		Δ_n^q	Δ_n^{Tq}	Classification R and Angle of Agreement Δ_n^R			
q	n	θ_p	ϕ_p	θ_p	ϕ_p			R	α_1	α_2	Δ^R
A		87.0	−4.5	Pos. S.							
		59.0	87.0								
		32.0	−100.5								
	1	81.0	65.5	22.0	23.0	31	40	B_3^4	6	7	8
		81.5	157.0	89.5	113.5			C_3^3	1.5	4.5	4.5
		12.0	−70.0	68.0	−157.0			D_{27}	2	11	11
	2	78.5	69.0	19.5	18.0	26	45	B_3^4	9	12	12
		81.0	161.0	87.5	116.5			C_3^3	5.5	6	7
		15.0	−74.0	70.5	−153.5			D_{27}	2	13	14
	3	63.0	4.5	15.0	75.0	25	47	B_1^1	11	14	15
		59.0	112.0	75.0	−115.0			C_9^2	7.5	8	10
		43.0	−118.0	87.0	−24.0			D_2	5	12	13
	4	84.0	11.5	21.0	44.0	26	38	B_1^1	9	12	13
		80.5	102.5	84.0	149.5			C_9^2	5	6	7.5
		11.0	−110.5	69.5	−118.0			D_{12}	5.5	11.5	12
	5	80.0	70.0	23.0	18.0	28	43	B_3^4	6	12	12
		80.5	162.0	86.5	116.5			C_3^3	6	6	8
		14.0	−64.0	68.0	−152.0			D_{27}	3	10	11
	6	68.5	63.5	25.0	42.5	35	37	B_3^4	5	6	6
		60.0	166.0	67.0	−161.0			C_3^3	3	4	5.5
		38.0	−57.0	80.5	−67.0			D_{18}	5	7	8
	7	65.0	63.5	22.5	37.0	32	38	B_3^4	5.5	6	7
		61.0	168.0	67.0	−159.0			C_3^3	1	2	2
		40.0	−60.0	84.0	−66.5			D_{18}	6	7.5	12
	8	38.0	79.0	31.0	90.0	32	36	B_2^3	6.5	7	8
		75.0	−171.0	70.0	−141.5			C_5^1	1.5	3	3
		56.0	−71.0	67.5	−43.5			D_{26}	4	12	12
	9	80.0	67.0	22.0	17.0	28	44	B_3^4	8	10.5	11
		80.0	159.5	87.0	114.5			C_3^3	4	6	7
		14.0	−65.0	69.5	−154.5			D_{27}	2	11	12
	10	38.0	68.0	33.0	85.5	32.5	30	B_2^3	7	8	10
		70.5	−174.5	69.0	−148.5			C_5^1	2	8.5	9
		59.0	−72.0	65.0	−49.0			D_{26}	6	9	10
	11	37.0	71.0	32.0	83.5	32	32	B_2^3	6	8	10
		73.0	−175.0	68.0	−147.0			C_5^1	4	7	7
		58.5	−74.0	67.0	−48.0			D_{26}	4	8.5	9
	12	39.0	75.5	31.5	89.0	32	35	B_2^3	6	7.5	8
		73.5	−172.0	70.0	−143.5			C_5^1	1	4	5
		57.0	−71.0	66.5	−45.5			D_{26}	3.5	11	11.5
	13	80.5	110.5	25.0	25.0	31	26	B_1^1	9	12	15
		89.0	−159.0	73.5	155.0			C_9^2	4	12.5	12.5
		9.5	−64.0	71.5	−109.5			D_{12}	6	12	12
	14	31.0	81.0	34.0	1.0	34	47	B_2^2	5	12	13
		61.5	−122.0	73.0	120.0			C_5^4	3	11	12
		80.0	−26.0	62.5	−141.0			D_5	3	7	7
	15	60.0	2.5	19.5	62.0	28	43	B_1^1	8	9	11
		62.5	110.0	89.0	155.5			C_9^2	3	4	4
		43.5	−126.5	70.5	−114.5			D_2	6	12	12.5
	16	81.0	65.5	22.0	25.5	31	40	B_3^4	6	7.5	8.5
		82.5	156.5	67.5	−156.5			C_3^3	2	3.5	4
		12.0	−75.0	89.0	−66.0			D_{21}	6	11	12
	17	44.0	61.5	15.5	30.0	24	37.5	B_3^4	9	11	15
		82.0	160.0	75.0	−154.0			C_3^3	4	6	8
		47.5	−102.5	88.5	−64.0			D_{21}	8	14	14
	18	77.0	71.0	18.5	17.0	24	47	B_3^4	10	14	15.5
		80.5	163.0	86.0	118.0			C_3^3	7	8	10
		16.0	−74.5	72.0	−151.0			D_{27}	6	14	15
	19	39.0	91.0	25.5	7.5	26	41	B_2^2	8	12	14
		55.0	−115.0	75.5	131.0			C_5^4	4	7	7
		77.0	−15.5	70.0	−133.5			D_5	8	12.5	13

TABLE 3.—*Recrystallization Data for Grains B, C, D, E, F and J in Specimen* D32, *Together with Analyses Made Using High-order Twin Groups*

Grain		Original Orientation		Rotated Group		$\Delta_n{}^q$	$\Delta_n{}^{Tq}$	Classification R and Angle of Agreement $\Delta_n{}^R$			
q	n	θ_p	ϕ_p	θ_p	ϕ_p			R	α_1	α_2	$\Delta_n{}^R$
B		87.0	5.5								
		57.0	99.5	Pos. S.							
		33.5	−88.5								
	1	60.5	66.5	18.5	21.0			B_3^4	5.5	8	10
		63.0	174.0	71.5	−162.0	32.5	39	C_3^3	5	5	6
		42.5	−62.0	89.0	−71.5			D_{21}	4	6	7
	2	64.0	70.0	25.0	32.5			B_3^4	2	2.5	2.5
		58.0	177.5	65.0	−162.5	37	34	C_3^3	3	4	5
		43.0	−50.5	85.0	−70.0			D_{21}	7	10	10
	3	55.5	14.0	23.0	68.0			B_1^1	6	6	6
		62.0	125.0	89.5	159.0	31.5	38	C_9^2	2	4	5
		47.5	−115.5	67.5	−110.0			D_3	5	7.5	9
	4	74.5	90.0	18.5	59.5			B_3^4	13	21.5	24
		17.0	−109.5	72.5	−141.5	19	40	C_1^2	10	15	17
		85.0	−1.5	83.5	−50.0			D_{19}	5	19	20
	5	61.5	13.0	20.0	40.5			B_1^1	9	10	13
		66.0	116.0	83.0	152.5	26	36	C_9^2	5	5	6
		38.0	−120.5	72.0	−115.0			D_{12}	4	12.5	13
	6	57.5	66.0	21.5	11.5			B_3^4	7	8	10
		61.0	176.5	88.0	108.0	31.5	38	C_3^3	2	8	8
		46.5	−62.5	69.5	−161.0			D_{21}	3	6	6
	7	41.0	71.0	15.0	34.0			B_3^4	9.5	11	14
		80.5	172.0	72.5	−153.5	25	40	C_3^3	4	7	8
		50.5	−90.5	87.0	−63.0			D_{21}	9	14	16
	8	84.5	22.0	19.0	42.0			B_1^1	11	11	14.5
		77.0	113.0	84.0	150.5	25	38	C_9^2	6	6.5	7
		14.0	−91.5	72.0	−118.0			D_{12}	5	14	14
	9	80.5	81.0	23.0	26.5			B_3^4	5	12	12
		82.0	172.0	89.0	117.5	28	44	C_3^3	3	6	6
		12.5	−61.5	67.5	−151.5			D_{27}	3	10	11
	10	74.0	29.0	10.5	73.0			B_1^1	7	16	17
		51.5	131.5	79.0	−109.0	28	38	C_6^4	6	7	7.5
		43.0	−79.5	81.5	−19.0			D_3	7	10	12
C		39.0	84.5								
		79.0	−171.0	Pos. S.							
		53.5	−72.5								
	1	66.0	66.5	30.5	82.0			B_2^3	5	10	10
		67.5	167.0	68.0	−145.0	30	31	C_5^1	4	6	6
		34.0	−65.0	70.0	−46.0			D_{26}	2	9	9
	2	56.5	53.0	28.5	51.0			B_1^1	4	7.5	8
		43.5	−172.0	82.5	154.0	35	37	C_7^3	3	5	5
		66.5	−54.0	62.0	−113.0			D_{12}	3	4	6
D		51.0	82.5								
		89.0	174.0	Pos. S.							
		39.5	−95.0								
	1	76.5	1.0	18.0	37.0			B_1^1	12	13	15.5
		36.5	110.0	82.5	149.5	23	36	C_9^2	8	8	8
		57.5	−98.5	73.0	−118.5			D_{12}	4	15	15
	2	82.0	103.5	32.5	40.0			B_1^1	7.5	12	13
		88.5	−166.0	77.5	150.5	35	31	C_7^3	4	6.5	9
		8.0	−67.0	61.0	−113.0			D_{12}	1.5	2	2
	3	31.0	51.0	24.5	17.5			B_3^4	6	12	13.5
		81.0	157.0	85.0	117.0	29	42	C_3^3	6.5	7	10
		61.0	−108.0	66.0	−151.0			D_{27}	4.5	8	10
	4	60.5	111.0	30.0	56.0			B_1^1	2	2.5	3.5
		52.0	−132.5	83.0	159.0	39	32	C_7^3	3.5	8	8
		52.0	−4.5	61.5	−107.0			D_{12}	4	8	8
E		62.0	80.0								
		89.5	170.0	Pos. S.							
		28.5	−99.5								
	1	70.5	59.5	23.0	41.0			B_3^4	5.5	7	7.5
		60.0	161.0	67.5	−158.0	31	39	C_3^3	1	3	3
		37.0	−58.0	83.5	−65.0			D_{18}	5.5	9	12
	2	84.0	3.5	15.5	56.5			B_1^1	12	13	20
		78.0	95.0	89.5	149.5	20	50	C_9^2	7	7.5	13
		13.0	−114.0	75.0	−120.5			D_3	9	16.5	18

TABLE 3.—(*Continued*)

Grain		Original Orientation		Rotated Group		Δ_n^q	Δ_n^{Tq}	Classification R and Angle of Agreement Δ_n^R			
q	n	θ_p	ϕ_p	θ_p	ϕ_p			R	α_1	α_2	Δ_n^R
F		56.0	82.5								
		83.0	177.5	Pos. S.							
		35.5	−83.0								
	1	74.0	62.0	23.0	54.0			B_3^4	8	9	12
		52.5	164.0	71.0	−162.0	32	29	C_3^3	4	9	9
		42.0	−47.0	77.0	−67.0			D_{13}	4	7	
		45.5	99.0								
		46.5	−102.0	Pos. S.							
		79.5	−1.0								
	1	45.5	59.5	24.5	17.0			B_3^4	2	6.5	7
		64.0	178.0	90.0	106.5	38	33	C_3^3	6	7	8
		56.0	−72.5	65.0	−164.5			D_{31}	4	5	6
	2	40.5	73.0	24.0	17.5			B_2^4	7	12	12
		73.0	−174.5	86.5	116.0	30	58	C_2^3	6	6	8
		55.5	−72.5	66.0	−152.0			D_{27}	3	9	10
	3	77.0	21.5	29.0	37.0			B_1^1	6	10	11
		77.0	114.0	77.0	153.0	32	30	C_7^3	8	9	9.5
		18.5	−112.0	65.5	−111.5			D_{12}	2	5	6

to show the appearance of two intersecting Neumann bands in a specimen of another heat of steel cold-rolled 4 per cent.

ANALYSIS AND INTERPRETATION OF RESULTS

Groups of Common Orientation

If the data of original orientations given in Tables 2 to 5 are plotted on stereographic nets, cases appear in which nearly the same orientations occur again and again. This situation may also be seen in a general way in a study of the tables themselves. For example, grains 1, 2, 5, 9, 16 and 18 of D32*A* in Table 2 form such a group. Orientations such as these may also be grouped together by means of small circles as shown in Figs. 5 and 6. In these illustrations the circles have the same angular radius (namely 5°) and the centers are 90° apart, conditions that permit treatment of the data on a probability basis.[2] The large numbers in Figs. 5 and 6 refer to individual states that are arbitrarily numbered. Consequently, each specimen must be treated independently of the other at this point in the analysis. Data of this type have been taken from Tables 2 to 5 and put into Table 6. The probability values for each sample have been calculated according to Eq. 2*a* of reference 2.*

However, some simplifications have been made in the data. For example, it was assumed for D32*A* that 20 orientations fell into 12 states, one having six orientations, another four; and the remaining ten, one each. Since actually there was a 6, 4, 2, 2, combination from 19 grains, the probability value given in the table is too large. The same statement applies for D2*B* where only the first three groups have been used. The total number of new grains considered for samples D32*B*, D53*A* and D2*B* are 10, 10 and 33, respectively; that is, the number of grains given in Tables 3, 4 and 5 for each of these samples. Finally, the value of N (i.e., the total number of states possible for a given value of α) used in Eq. 2 was 1000, a value that is too small for α equal to 5°. This again makes all the probability values in the table too high.

According to the probabilities given in Table 6, one would scarcely expect to find any states as highly populated as those actually obtained if orientation changes had taken place in a haphazard manner.

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* Numerical illustrations are given in Table 2, page 219 of that paper.

TABLE 4.—*Recrystallization Data for Grain A in Specimen* D53 *with Complete Recrystallization in Area Investigated; also Some Grain-boundary Nucleations in Specimens* D32 *and* D1

Grain		Original Orientation		Rotated Group		Δ_n^q	Δ_n^{Tq}	Classification R and Angle of Agreement Δ_n^R			
q	n	θ_p	ϕ_p	θ_p	ϕ_p			R	α_1	α_2	Δ_n^R
D53-*A*		85.0	5.0								
		43.0	100.0	Pos. S.							
		48.0	−89.0								
	1	61.0	81.0	24.0	5.0			B_2^2	10	12	15
		86.5	173.0	76.0	130.5	24	44	C_5^4	7	8	9
		30.0	−91.0	71.0	−134.5			D_8	8	14	14
	2	59.0	101.5	17.0	56.0			B_1^1	10	14	18
		84.5	−164.5	89.0	148.5	21	50	C_9^2	5	10	10.5
		32.5	−66.0	73.5	−121.5			D_3	8	19	19
	3	72.0	21.0	30.5	85.0			B_2^3	5	8	8
		69.0	118.0	69.0	−142.0	31	36	C_5^1	3	3	4
		28.5	−106.5	70.0	−43.5			D_{26}	2	10	10
	4	60.0	94.0	18.0	34.5			B_3^4	8	9	14
		36.0	−122.0	72.0	−152.5	25	40	C_3^3	4	5.5	7
		73.0	−6.0	88.0	−62.0			D_{18}	9.5	13	15
	5	68.0	22.0	34.0	86.0			B_2^3	6	7	8
		71.5	120.0	69.0	−146.0	36	32	C_5^1	5	6	6
		30.0	−114.0	66.0	−46.0			D_{26}	3.5	9	10
	6	71.0	18.0	27.5	3.0			B_2^2	6	10	11.5
		30.5	143.0	71.0	134.0	28	36	C_5^4	3	5	5
		67.0	−80.5	70.5	−129.5			D_8	3	12	12.5
	7	30.5	72.0	20.0	6.0			B_3^4	13	15	16
		59.0	−109.5	83.0	116.0	23.5	58	C_3^3	8	10	11
		89.0	−18.5	72.0	−151.0			D_{27}	12	15	15
	8	73.0	16.0	29.0	11.0			B_2^2	4.5	12	12
		27.0	142.0	74.0	133.5	30	38	C_5^4	1	6	6.5
		70.0	−81.0	68.0	−129.5			D_8	4	9	11
	9	19.0	96.0	23.5	53.5			B_1^1	5	9	10
		85.0	−159.0	86.0	152.5	29	40	C_9^2	2	4	4
		72.0	−67.0	67.0	−115.5			D_{12}	7.5	8.5	11
	10	53.0	71.0	21.0	67.0			B_1^1	5	18	19
		71.0	176.5	67.0	−125.0	25	40	C_9^2	5	12.5	13
		44.0	−72.0	85.5	−33.0			D_9	9	9	13.5
D32-1$_c$		56.0	65.5								
		62.5	176.0	Pos. S.							
		46.5	−64.0								
	A	87.0	−4.5	26.0	40.5			B_1^1	8	9	12
		59.0	87.0	79.0	150.5	32	29	C_9^2	4	7.5	9
		32.0	−100.5	66.0	−115.0			D_{12}	1.5	7	8
	F	56.0	82.5	16.0	37.0			B_1^1	13	14	18.5
		83.0	177.5	83.5	147.5	20	38	C_9^2	8	10	12
		35.5	−83.0	75.0	−120.5			D_{12}	6.5	18	18
	H	44.5	88.5	23.0	74.0			B_1^1	8	8	11
		46.0	−97.0	66.0	−114.5	31	40	C_9^2	3	7	7
		87.0	−4.0	87.0	−24.0			D_9	3.5	9	11
D32-2$_c$		62.5	1.5								
		50.0	117.5	Pos. S.							
		52.5	−113.0								
	D	51.0	82.5	27.0	74.0			B_1^1	7	14	14
		89.0	174.0	64.5	−120.0	30	42	C_9^2	9	10	10
		39.5	−95.0	85.0	−28.0			D_9	6	7	9
	K	90.0	2.0	20.0	75.0			B_1^1	10	10	12
		50.0	91.0	70.5	−115.0	27	44	C_9^2	5	7	7
		40.0	−88.0	87.5	−24.0			D_8	2	11	12
D32	I	34.0	106.0								
		57.0	−66.0								
		86.5	−158.0								
	II	56.0	70.0								
		70.0	174.5								
		41.0	−71.0								
	III	(Same as D32-1$_c$ above)									
D1-1$_c$		75.5	18.0								
		71.5	113.0	Pos. S.							
		23.0	−107.5								
	A	89.0	0	30.5	33.0			B_3^4	4	5	6
		38.0	91.5	60.0	−159.5	38	33	C_3^3	2	8	8
		52.0	−91.0	84.0	−67.0			D_{27}	5	6	7
	B	54.5	87.0	15.0	50.0			B_3^4	2	14	14
		88.0	178.0	77.0	−161.0	28	35	C_4^1	6	6	8
		35.0	−89.5	82.0	−69.5			D_{13}	5.5	7.5	9

TABLE 5.—*Recrystallization Data for Grain B in Specimen* D2, *Nucleation and Growth Occurring among Neumann Bands*

Grain		Original Orientation		Rotated Group		Δ_n^q	Δ_n^{Tq}	Classification R and Angle of Agreement Δ_n^R			
q	n	θ_p	ϕ_p	θ_p	ϕ_p			R	α_1	α_2	Δ_n^R
B		45.0	90.0								
		88.0	−178.0	Pos. S.							
		45.0	−86.5								
	1	76.0	21.5	24.0	73.0			B_1^1	7	7	8.5
		28.0	139.5	66.5	−111.0	32	40	C_9^2	2	7	7
		66.5	−75.0	88.5	−20.5			D_3	5	8	8
	2	80.0	14.0	17.0	63.0			B_1^1	11	13	16
		31.0	121.0	73.0	−118.5	23	48	C_9^2	7	7	8
		61.0	−82.0	89.5	−28.0			D_3	6	12.5	16
	3	76.0	110.0	39.0	19.0			B_2^2	12	12	14
		76.5	−156.0	66.5	142.0	38.5	26	C_8^1	3	14	14
		20.0	−24.5	61.0	−114.5			D_8	1	6.5	6.5
	4	31.5	94.0	28.0	76.5			B_2^3	5	13	13
		62.5	−114.0	66.5	−138.5	28	39	C_5^1	2	7	8
		77.5	−17.0	76.0	−42.5			D_{23}	10	10	10
	5	79.0	16.0	17.0	63.5			B_1^1	11	15	16
		32.0	124.5	74.0	−116.0	24	46	C_9^2	5	6.5	7
		61.0	−81.0	90.0	−26.0			D_3	6	12	13.5
	6	24.5	79.0	29.0	85.5			B_2^3	8	10	12
		66.0	−110.5	71.0	−146.5	29	32	C_5^1	4	8	8
		86.5	−18.5	68.5	−49.0			D_{26}	3	12	12
	7	28.0	100.5	30.0	82.0			B_2^3	6	9	10
		65.5	−112.5	66.0	−137.0	30	41	C_5^1	4	4	5
		76.5	−16.5	73.0	−39.0			D_{23}	6	7.5	9
	8	87.0	28.0	34.0	0.0			B_2^2	5	19	19
		18.0	125.5	60.5	148.5	34	23	C_5^4	3	18	18.5
		72.0	−63.5	76.0	−113.0			D_8	10.5	19	19
	9	24.5	87.0	25.0	77.0			B_2^3	8	14	16
		83.0	−166.0	69.0	−135.5	25	42	C_5^1	4	9	10
		67.0	−73.0	77.5	−40.0			D_{23}	8	12	12.5
	10	86.0	20.5	22.0	40.0			B_1^1	10	11	12
		67.0	112.0	81.0	152.5	27.5	34	C_9^2	4	6	9
		23.5	−79.0	70.5	−114.0			D_{12}	2.5	11	12.5
	11	37.0	58.5	26.0	54.0			B_3^4	8	10	10
		89.0	150.5	68.0	−158.5	32	30	C_3^3	0.5	9	9
		53.0	−119.0	77.0	−63.0			D_{18}	2	8	8.5
	12	82.0	25.0	25.0	87.5			B_1^1	10	12	16
		26.0	131.5	67.0	−115.5	30	42	C_9^2	4	12	14
		65.5	−68.0	81.0	−21.5			D_9	9	10	12
	13	78.5	19.0	24.0	60.5			B_1^1	3.5	7	7
		71.0	113.0	88.0	156.5	30	38	C_9^2	2.5	2.5	3
		22.5	−101.0	66.0	−112.5			D_9	3	10	10
	14	72.0	67.0	25.0	47.5			B_3^4	7	7	8
		81.5	160.0	67.5	−159.0	33	36	C_3^3	2	6	6
		20.0	−86.0	79.5	−65.0			D_{18}	3	8	8
	15	61.0	78.0	15.0	54.0			B_3^4	14	17	20
		84.5	171.0	76.0	−146.5	18	40	C_3^3	10	12	15
		30.0	−90.0	85.0	−55.0			D_{18}	10	18	20
	16	72.5	21.0	21.0	73.0			B_1^1	7	7.5	8
		70.0	118.0	69.0	−108.5	33	38	C_9^2	3	6	7
		28.0	−107.0	89.0	−18.0			D_3	2	6	6
	17	70.5	66.5	25.0	53.0			B_3^4	8	9	10
		83.0	159.0	69.5	−159.0	32	31	C_3^3	2	8	8
		21.0	−93.0	78.0	−64.5			D_{18}	2	9	10
	18	73.5	73.0	26.0	27.0			B_3^4	3	8	10
		74.5	167.5	64.5	−154.5	31	40	C_3^3	4	4	5
		23.0	−61.0	89.5	−64.5			D_{27}	2	7	8
	19	49.0	68.0	23.0	29.0			B_3^4	5	12.5	12.5
		42.5	−119.5	67.0	−151.0	28	44	C_3^3	1.5	7	7
		86.0	−25.0	90.0	−61.0			D_{27}	4	8	10
	20	52.5	64.0	29.0	18.5			B_3^4	6	10	12
		38.5	−130.0	86.5	115.0	34	43	C_3^3	8	9	10
		83.5	−21.0	61.0	−153.5			D_{27}	2.5	4	4
	21	23.0	86.0	27.5	7.0			B_2^2	8	11	12
		67.5	−105.0	75.0	128.5	28	42	C_5^4	4.5	6	8
		85.5	−13.0	68.0	−135.0			D_5	5	11	11
	22	30.0	52.5	22.0	40.0			B_3^4	7	11	12
		74.0	173.5	69.0	−152.0	28	40	C_3^3	3	6.5	8
		66.0	−90.0	86.0	−60.5			D_{18}	8	11.5	11.5
	23	28.0	77.5	22.0	79.0			B_2^3	9	14	18
		78.0	−169.0	72.0	−140.0	22	38	C_5^1	4	9	11
		65.0	−74.0	75.0	−46.0			D_{26}	15	15	16

TABLE 5.—(*Continued*)

Grain		Original Orientation		Rotated Group		$\Delta_n{}^q$	$\Delta_n{}^{Tq}$	Classification R and Angle of Agreement $\Delta_n{}^R$			
q	n	θ_p	ϕ_p	θ_p	ϕ_p			R	α_1	α_2	$\Delta_n{}^R$
	24	57.5	60.5	34.5	5.5	40	33	$B_3{}^4$	8	13	16
		34.5	−138.5	83.5	106.0			$C_3{}^3$	11	13	18
		81.0	−35.0	57.0	−159.5			D_{27}	4	10	11.5
	25	38.0	48.0	16.0	31.0	28	44	$B_3{}^4$	5	5	13
		70.0	167.0	75.0	−159.0			$C_3{}^3$	1	6	7
		60.0	−91.0	87.0	−68.0			D_{13}	6.5	11	12
	26	89.0	25.5	24.5	29.0	30	28	$B_1{}^1$	10	11	13
		67.0	116.0	75.0	154.0			$C_9{}^2$	3	11	11
		23.0	−66.5	71.0	−111.0			D_{15}	6.5	10	12
	27	26.0	56.0	34.0	71.0	34	22	$B_2{}^3$	12	15.5	20
		89.0	149.0	67.0	−159.0			$C_5{}^1$	10	16	18
		64.0	−120.0	66.5	−59.0			D_{18}	8	12	12
	28	70.0	69.0	22.0	41.0	30	36	$B_3{}^4$	7	7	9.5
		79.0	163.5	69.0	−157.0			$C_3{}^3$	2	3	4
		24.0	−81.0	83.5	−64.0			D_{18}	5	10	12
	29	70.0	73.0	23.0	37.5	28	39	$B_3{}^4$	6	10	12
		79.0	167.0	68.0	−153.0			$C_3{}^3$	2	5	5
		24.0	−76.5	86.0	−61.5			D_{18}	7	11	11
	30	73.0	66.0	26.0	49.5	35	26	$B_3{}^4$	4	8	8
		83.0	158.0	66.5	−161.0			$C_3{}^3$	3	8	9
		19.0	−91.5	77.0	−66.0			D_{18}	4	7	8
	31	74.5	70.5	28.0	51.5	33.5	31	$B_3{}^4$	7	8	11
		85.0	161.5	64.5	−157.5			$C_1{}^2$	8	8	8
		17.0	−93.0	78.0	−62.0			D_{18}	1	6	6
	32	49.0	70.0	21.0	27.5	25	47	$B_3{}^4$	7	14	15
		42.0	−117.5	89.0	120.0			$C_3{}^3$	3	8	8
		86.0	−23.0	68.5	−149.0			D_{27}	5.5	12.5	13
	33	11.0	69.0	35.0	40.5	35	44	$B_3{}^4$	9.5	21	22
		85.5	−179.0	55.0	−142.0			$C_1{}^2$	4	9	9
		80.0	−88.0	89.0	−51.0			D_{17}	2.5	9	9

Consequently, their occurrence is a very strong indication that a definite type of transformation did take place during the recrystallization of the samples of silicon ferrite. Our problem, therefore, is to obtain a further classification of the data if this is at all possible, in order to uncover some reasonable type of transformation.

TABLE 6.—*Distribution of New Grains or Nuclei in States (Size 5°) Each with Two or More Orientations for Samples* D32*A*, D32*B*, D53*A* *and* D2*B* *and Probabilities of Occurrence of Any Such Groups*

Sample	State	Nuclei	Probability
D32*A*	1	1, 2, 5, 9, 16, 18	3.6×10^{-17}
D32*A*	2	8, 10, 11, 12	
D32*A*	3	3, 15	
D32*A*	4	6, 7	
D32*B*	1	3, 5	2.5×10^{-6}
D32*B*	2	1, 6, 2	
D53*A*	1	3, 5	6.1×10^{-4}
D53*A*	2	6, 8	
D2*B*	1	14, 17, 28, 29, 30, 31	1.8×10^{-15}
D2*B*	2	1, 2, 5	
D2*B*	3	4, 6, 7	
D2*B*	4	19, 20, 32	
D2*B*	5	8, 12	
D2*B*	6	10, 26	
D2*B*	7	13, 16	
D2*B*	8	9, 23	
D2*B*	9	22, 25	

Comparison with High-order Twins

Standard groups of twins through four orders have been calculated for use in the analysis of recrystallization data,[4] and these will be used in the present work in the way described under the section headed "Some General Applications," ref. 4.

Data on orientations of rotated groups made with a Wulff net are listed in Tables 2, 3, 4 and 5 under the heading "Rotated Group." The grain that is rotated into the fourfold symmetry position "Pos. S" (usually an old grain and designated by a letter) precedes the other members of the group. Fig. 8 illustrates a plot of grain *A* in specimen D32. In this case comparison with Fig. 2 in ref. 4 shows at once that there is some agreement with the third-order orientations. To illustrate this, we locate C_3^3, C_9^2, C_5^4, and C_5^1 on the plot in Fig. 8, making each into a state of 5° radius. It can be seen that grain 6 falls very near state C_3^3, that three orientations do fall into this state, and that grains 10 and 11 fall very near state C_5^1. Altogether, six orientations fall into three of the four states. It will be pointed out later that these six orientations also belong to one general class.

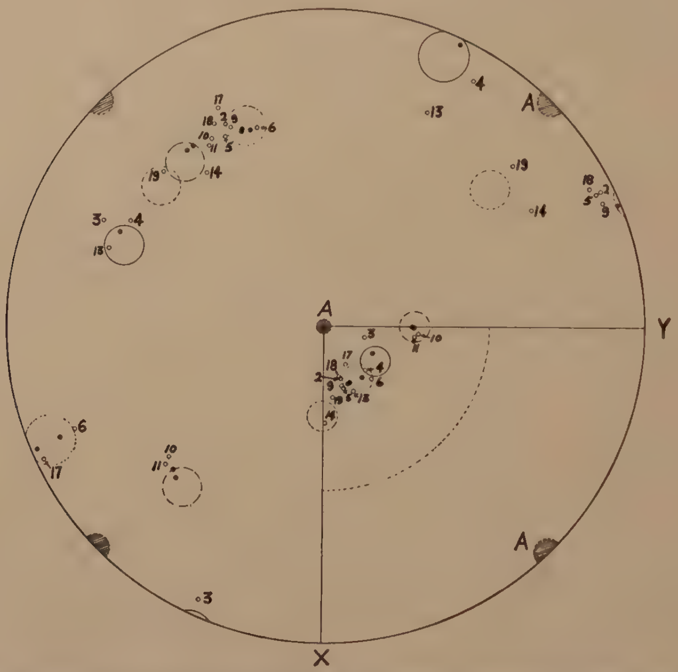

FIG. 8.—STEREOGRAPHIC PROJECTION OF GRAIN *A* AND 19 NUCLEI OF SPECIMEN D32 AFTER ROTATIONS INTO STANDARD POSITION.

Orientations falling into third-order twin states (size 5°) of the C_3 class are indicated by black dots. Other orientations are numbered according to nuclei.

Before a complete analysis of all the samples is made, it is worth while to consider the question of amount of difference in orientation between two grains, say *A* and *B*. To do this, the cube poles of each orientation are plotted on a stereographic net. Those of grain *A* are then enclosed with circles of radius Δ_B^A degrees, a value just large enough to include all the cube poles of *B*. In the present work Δ_B^A will be used to indicate the amount of difference in orientation between *A* and *B*. If there is a change in orientation on recrystallization, designated in our tables by Δ_n^q, the value of this number gives an idea of the amount of change in orientation while going from grain *q* to nucleus *n*. Similarly, the difference in orientation between the new grain *n* and the nearest twin of *q*, call it *Tq*, may be indicated by the number Δ_n^{Tq}. In the case of second-order, third-order and fourth-order twins, the particular twin orientation that is nearest to the new grain will be selected to determine the numbers Δ_n^R, *R* standing for *B*, *C* and *D*, as indicated in the tables. Although the number Δ_n^R would suffice in the present work, values for one-pole and two-pole agreement have been put in the tables under the columns headed α_1 and α_2, respectively, since these numbers were also obtained. Values for $\Delta_n{}^q$, $\Delta_n{}^{Tq}$, α_1, α_2, and $\Delta_n{}^R$ that were obtained for every case of recrystallization are listed in tables 2, 3, 4 and 5.

The first thing to note is that the change in orientation $\Delta_n{}^q$ during recrystallization is fairly large, the average value being about 29.5° and the minimum value being 18°. The values of $\Delta_n{}^{Tq}$ indicate also that each of the new orientations is far removed from that of a first-order twin of the parent grain. Better agreement, however, is found among second, third, and fourth-order twins. In general, the agreement is better for third-order twins than it is for fourth-order twins, but this will be discussed more fully later.

It has been pointed out in ref. 4 that the system of four orders of twins can be reduced to nine general classes that include one from the first, one from the second, two from the third and five from the fourth. It would, therefore, be better to reduce the classifications in Tables 2 to 5 to the nine general classes, since old grains were put into position S in a somewhat arbitrary manner. The reclassified data may be put into a table showing the distribution of orientations among the nine classes according to closeness of fit (i.e., according to $\Delta_n{}^R$ being less than an arbitrarily chosen number α, which fixes the size of each state). Results of this type appear in Table 7 for each sample for five values of α.

These results are very interesting because no orientations according to best fit fall into states A, D_{22} and D_7. Out of a total of 84 orientations, only one falls into state D_{24} and this one drops out at α equal to 7°. Furthermore, the distribution according to first, second, third, and fourth-order classifications does not turn out according to their relative weights, which are 1, 3, 9 and 27, respectively. The distributions for α equal to 10°, 7° and 5° are in that order: 0, 30, 68 and 32; 0, 7, 37 and 11; and 0, 2, 17 and 2. There is little doubt that the data fit third-order twin orientations better than they do fourth-order ones.

It is very interesting to compare the arbitrary classifications of Table 6 with those obtained from Tables 2, 3, 4 and 5, the very best case of agreement being selected. For example, state 1 of D32*A* of Table 6 contains grains 1, 2, 5, 9, 16 and 18. In Table 1, however, it is shown that the best fit among four orders of twins for each of these grains is $C_3{}^3$ (this is a C_3 state in our general class of nine). One might say therefore that state 1 and state $C_3{}^3$ are related, since the data can be correlated with either of them. State $C_3{}^3$ would have to have a radius of 10° to include all six orientations, whereas state 1 does this with α equal to 5°. Continuing with states 2, 3 and 4 of Table 6, sample D32*A*, one finds from Table 2 that grains

TABLE 7.—*Distribution of Orientations among the Nine General Classes for Five Values of α (Expressed in Degrees)*

n gives the number of recrystallization nuclei per old grain or grains

Specimen	Number of Orientations According to Class										
	α	n	A	B	C_3	C_4	D_{24}	D_{22}	D_{21}	D_{15}	D_7
D32*A*	15	19	0	18	19	0	0	0	10	9	0
D32*A*	10	19	0	8	17	0	0	0	2	2	0
D32*A*	7	19	0	2	11	0	0	0	1	0	0
D32*A*	5	19	0	0	6	0	0	0	0	0	0
D32*A*	3.5	19	0	0	2	0	0	0	0	0	0
D32*B*, *C*, *D*, *E*, *F* and *J*.	15	22	0	18	16	5	0	0	14	5	0
D32*B*, *C*, *D*, *E*, *F* and *J*.	10	22	0	9	15	5	0	0	9	4	0
D32*B*, *C*, *D*, *E*, *F* and *J*.	7	22	0	4	8	1	0	0	6	0	0
D32*B*, *C*, *D*, *E*, *F* and *J*.	5	22	0	2	3	1	0	0	1	0	0
D32*B*, *C*, *D*, *E*, *F* and *J*.	3.5	22	0	2	1	0	0	0	1	0	0
D53*A*	15	10	0	7	10	0	0	0	3	6	0
D53*A*	10	10	0	3	7	0	0	0	0	2	0
D53*A*	7	10	0	0	6	0	0	0	0	0	0
D53*A*	5	10	0	0	3	0	0	0	0	0	0
D53*A*	3.5	10	0	0	0	0	0	0	0	0	0
D2*B*	15	33	0	23	27	3	1	0	17	11	0
D2*B*	10	33	0	10	23	1	1	0	9	5	0
D2*B*	7	33	0	1	11	0	0	0	2	2	0
D2*B*	5	33	0	0	5	0	0	0	0	1	0
D2*B*	3.5	33	0	0	1	0	0	0	0	0	0
Sum of above	15	84	0	67	72	8	1	0	44	31	0
	10	84	0	30	62	6	1	0	20	11	0
	7	84	0	7	36	1	0	0	9	2	0
	5	84	0	2	16	1	0	0	1	1	0
	3.5	84	0	2	4	0	0	0	1	0	0

8, 10, 11 and 12 belong best to a C_3^1 state; grains 3 and 15 to a C_3^2 state; and 6 and 7 to a C_3^3 state (it must be remembered that special rotations were carried out to obtain Fig. 8 and the data of Tables 2 to 5; so states 1 and 4 of Table 6 have come together at the position of C_3^3). In any case, these states belong to the C_3 class. Consequently, all 14 grains may be put into a single classification—one corresponding to a third-order twin orientation. (The C_3 group is only one half the size of the C_4 group; so the data really fit a special subset of the third-order twin group.)

Even more remarkable is the fact that all the orientations of nuclei listed in Table 6, with the exception of grain 31 of sample D2*B*, fit the C_3 class better than any other one. Grain 31 deviates from C_3 by only 10° and this is less than the deviation for grains 8 and 12 of D2*B*. The average deviation from C_3 for all the grains is only about 7°. Orientations that did not fall into groups also can be found in Tables 2 to 5 that fit the C_3 class best. Since the probabilities given in Table 6 were calculated on the basis of no restrictions as to particular orientations, one should feel safe in saying that the present data fit a C_3 classification remarkably well. However, the fact that there is also good agreement among second-order twin orientations must not be overlooked. In this connection, there is a definite correlation between the type of distribution shown in Table 7 and the relative positions of these orientations as shown in Figs. 2, 3 and 4 of ref. 4. For example, the orientations that are nearest to C_3^3 are B_3^4, (C_4^1, D_{13}), D_{18} and D_{21}, the difference in orientation being about 8°, 11°, 11.5° and 12.5°, respectively. Those nearest to B_3^4 are C_3^3 and (C_4^1, D_{13}, D_{18} and D_{21}) at about 8° and 11°, respectively. However, in terms of our general classifications, all those orientations or states reduce to B, C_3 and C_4, D_{15} and D_{21}, the ones that are more highly populated in Table 7. Consequently, if recrystallization should occur according to inexact second-order (B) or third-order (C_3) twins, one would expect to find some data fitting B better than C_3, and vice versa, and some even fitting C_4, D_{15} or D_{21} best if the degree of inexactness should become fairly large.

Even in cases of grain-boundary nucleation given in Table 4, it may be noted that a C_3 classification generally fits the data best. However, $D_{1\text{-}1_6}$ could be classified better as a second-order twin transformation if it nucleated according to the matrix of grain *A*. Some evaluation of data for single cases of nucleation can be made because if a single nucleation takes place within a grain in a haphazard manner, the probability that it is one of the 52 first, second, and third-order twins to within 5° is about 1/22 (see refs. 2 and 4). However, the probability that it is also in the C_3 class would be 1/22 × 3/13, or about 1/95. This figure also applies to the second-order twin class.

Finally, it may be pointed out that all parts of a Neumann band need not be in exact twin relation to the average orientation of the parent grain. Fig. 7 shows a Neumann band bent at the intersection point of two bands. The angular shift, measured in the plane of the microsection, amounts to about 6° for the case illustrated. Also, it has been pointed out previously[3] that the spread in orientation of the main grain near a Neumann band is greater than in regions apparently free of such bands. These variations all taken together could easily throw the orientation of a second-order mechanical twin out of exact angle relationship with the old grain, especially if such a twin were formed in a bent portion of a Neumann band.

Although second-order twins have been observed in antimony[5] and zinc,[6] they have not been observed in silicon ferrite. Nevertheless, the assumption that they may be formed is attractive if we wish to account for nuclei that are near second-order or third-order twins of the parent grain. This, incidentally, would be only one or two steps beyond nucleation according to a first-order twin; and, in this connection, it has been observed in the case of early transformations in grains of silicon ferrite containing Neumann bands of the type shown in Figs. 3 and 7 that these bands do grow a small amount (i.e., enlarge 50 per cent or so) in certain areas of the sample whereas in other areas they are absorbed by the old grain. However, in a second anneal at higher temperatures they are completely removed, either by the old grain as it undergoes recovery or by growth of another grain.

DISCUSSION AND CONCLUSIONS

It has been shown on the basis of probability calculations that a considerable number of data on orientation changes cannot be accounted for in a reasonable way if no specific mechanisms are involved during recrystallization of silicon ferrite crystals. However, the same data do fit a second-order or a third-order twin relationship remarkably well and a fourth-order twin relationship rather poorly. In fact, the fit is best with a special third-order twin class that is a small subgroup of all third-order twins, a group of the same size as the one of second-order twins. Incidentally, this special subgroup corresponds to orientation changes that can be classed as "single axis of rotation type."[4]

It was also pointed out that certain natural deformations within a grain could produce a spread in the orientation changes if nucleation should occur according to second-order or third-order twin transformations essentially of mechanical origin. Although the amount of spread allowable is not known, it might be as high as 10°. Table 7 shows that there are 16 cases out of 84 that fall outside the 10° range, and nine of them come from sample D2. Although the presence of large Neumann bands in this sample may have a spreading effect on the distribution of orientations, there are, nevertheless, cases such as grain 4 of D32*B*, in which no bands were observed and the deviation still is large. Furthermore, the present material, although relatively free of inclusions, is not completely ideal to represent a crystalline lattice, therefore, probably it would be logical to expect to find some data of a misfit type. In any case, 80 per cent of the data can be classified so as to show excellent agreement with third-order twin transformations.

ACKNOWLEDGMENT

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The Orientation Texture at the Surface of Cast Metals

By Gerald Edmunds,* Member A.I.M.E.

(Cleveland Meeting, October 1944)

In a paper[1] before this Institute in 1940, the writer reported that the surface orientation texture of zinc and cadmium differed from the texture existing within the casting, in that basal planes were parallel to the surface. He was unable to rationalize the origin of this surface texture.

It is conceivable that the surface orientation texture is influenced by the atomic force fields, which are different at the surface and within the body of metal. It was considered that a radical change in the surface against which the metal is cast might alter the surface texture.

In trial of this, zinc has been cast against a surface of molten lead, but the same result has been obtained—i.e., (001) parallel, ±20°, to the surface—as was obtained when it was cast against air, Transite or iron.[1]

Into the bottom of an open cast-iron tray, 7 by 14 in. by 2 in. deep, preheated to about 275°C., about ¼ in. of lead, then ½ in. of zinc was poured, and the whole was covered with an electric heater to enforce freezing from the bottom upward. After a lapse of time sufficient for the zinc but not the lead to solidify, the zinc slab was raised free of the molten lead. The bottom surface of the zinc casting was coated with a thin layer of lead. A specimen of the slab 1½ in. square was metallographically polished to flatten it and remove the slight film of lead, and the orientation was determined by the method used before,[1] with the result stated above.

Some determinations have also been made on other metals, as follows:

Surface orientation determinations were made on the ⅝-in. diameter grip section of two ¼-in. diameter aluminum-alloy die-cast tensile bars and on a ⅛ by ½-in. flat aluminum-alloy die-cast tensile bar. None of these three aluminum die castings exhibited any preferred orientation at the surface.

A brass die casting (nominal composition: 60 Cu, 37.75 Zn, 1.00 Sn, 1.00 Pb, 0.10 Al, 0.15 Si) furnished by C. S. Smith was also examined. The surface showed a random orientation of alpha and beta.

Summary

A zinc casting solidified against a molten lead surface was found to have the same surface orientation texture, (001) parallel to the surface, as other zinc and cadmium castings.

Aluminum and alpha-beta brass die castings were found to have random grain orientation textures at the surface.

Acknowledgment

The X-ray determinations were conducted by M. L. Fuller.

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[1] G. Edmunds: Grain Orientation of Cast Polycrystalline Zinc, Cadmium and Magnesium. *Trans.* A.I.M.E. (1941) **143**, 183–197.

DISCUSSION

(*Paul A. Beck presiding*)

F. M. WALTERS, JR.*—How thick was the external layer compared with the other orientation on the inside?

G. EDMUNDS.—Do you mean on the casting made against molten lead?

F. M. WALTERS, JR.—In any case.

G. EDMUNDS.—We did not determine the thickness of the surface orientation texture on zinc cast against molten lead. In the previous paper,[1] the layer on chill castings was shown to be of the order of 1/16-in. thickness, with considerable difference for the several castings examined. On the only die casting reported (very rapidly cooled), the surface orientation was less than 0.009 in. thick.

P. A. BECK.†—Crystal orientation and directional growth are very important in certain types of castings. Apparently cubic metals and alloys do not show the skin effect Mr. Edmunds found in hexagonal metals, and any explanation of the effect in zinc should have to take this fact into consideration.

MEMBER.—What would be the practical aspect of this orientation on the surface? Would it be different from the interior of the casting? Would that weaken the surface of the casting at all, such as zinc-alloy die casting?

G. EDMUNDS.—The surface orientation texture would not be expected to weaken the surface of a die casting. Deformation by extension parallel to the basal planes can result in twinning of the hexagonal structure; hence, there is a mode of deformation available at the surface. I have nothing definite to offer regarding the influence of this orientation on other properties. One can well imagine that there is a very decided influence on corrosion characteristics; for example, because it is well known that the corrosion characteristics and electrode potentials vary as a function of the exposed atomic plane.

I do hope one of you will try to offer an explanation for the existence of this surface effect.

B. W. GONSER.*—I am sorry not to be able to offer an explanation. Instead, I want to ask if you think it would be of any advantage or disadvantage for alloy additions to be made as long as the structure remains the same? Would the same effect occur or would it be modified, become thinner, or change in some way?

G. EDMUNDS.—Mr. Gonser has raised an interesting point. Solid-solution alloying in hexagonal metals changes the axial ratio. Cadmium and zinc have large axial ratios as compared with magnesium, titanium and other hexagonal metals, and this difference in axial ratios influences the orientation of the columnar grains within the body of the casting, as was shown in the earlier paper.[1] Aside from primary solid solution phases, some intermediate alloys have the hexagonal close-packed structure. The epsilon phase of the zinc-copper system is an example of one having an axial ratio nearer that of magnesium than zinc. It would be interesting to know the orientation texture of castings of this phase. In our one attempt to study this we obtained a poor casting, and did not make the texture determinations.

We do not know whether the surface orientation depth would be affected by alloying. In the particular cases studied[1] a number of different grades of zinc were used, involving minor impurities commonly present in some grades of commercial zinc, and no influence of these impurities was detected.

F. M. WALTERS, JR.—Mr. Edmunds, you have been thinking about this for four or five years and I have been thinking of it for five minutes. I would say if you picture atoms as balls and drop them down on the surface, it is going to be easier for them to arrange themselves in the hexagonal pattern than to lay themselves out in other ways, so the question becomes not why they have the hexagonal phase on the surface but perhaps why they change so quickly.

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* Battelle Memorial Institute, Columbus, Ohio.

G. Edmunds.—I think Dr. Walters is thinking of something that I have thought of for four or five or six years. The surface tension of metals is to me an indication that the surface atom density is attempting to reach a maximum, and, of course, the maximum of density is the formation of the hexagonal arrangement, such as the basal plane in zinc. You might imagine the surface-tension structure is frozen in place. That is just about as far as my speculation has carried me.

C. E. Swartz.*—I would like to ask just two questions. The first one is: What is the effect of temperature upon this phenomenon, if any, and in the event there is no effect upon temperature or temperature upon it (I am speaking now of mold temperature rather than metal temperature), what would happen if one were to galvanize, so to speak, a mold of steel and have the mold temperature above the melting point of zinc and then cast the zinc into the mold, cut a section and study the orientation from let us say pure iron to pure zinc or cadmium? Cadmium might be a little more difficult because an intermediate bonding alloy must be used.

G. Edmunds.—Various mold temperatures were used. In the original experiments[1] the casting against an air surface constituted a condition very different from chill casting in an iron mold. Also, when metal is poured into a Transite or graphite mold, the surface may freeze but remelt and the effective mold temperature would be very high. So I think we really have explored quite a range of mold temperatures without effect.

As to the second question—on the idea of galvanizing the mold—perhaps there would be a relationship between orientation of the zinc and zinc-iron phase. Whether that would continue on into the zinc would have to be determined by experiment.

I do not believe the case would be particularly valuable to investigate. Do you have something in mind that I don't understand?

C. E. Swartz.—No, the thought occurred to me while you were talking that if it were possible to bring about some condition entirely different from anything you had previously described, maybe it would be so far away from the data you have that you would be forced to draw a correct conclusion, so to speak; and it occurred to me that there would be quite a difference between any surface you had previously described and a surface of the metal itself, assuming that you were able to put a galvanized coat on so thick that the iron impurity would be no greater than the iron impurity in, say, Prime Western. I think that would be possible—I don't know—but if it were possible, what would be the orientation of the zinc crystals beginning at the point where the iron content becomes that of the metal? That is my thought now, it may have no value.

G. Edmunds.—That is at the point where the zinc phase is distinct from the zinc-iron intermetallic phase?

C. E. Swartz.—That is right.

G. Edmunds.—It would be interesting to try the experiment.

C. E. Swartz.—I don't know much about this. Obviously, I am like Dr. Walters—I have been thinking about it for a few seconds, but you have a crystallization tendency perhaps caused by the crystallization of your zinc-iron phase. What is that going to do to the tendency of your relatively pure zinc phase?

G. Edmunds.—I am just unable to answer you, Dr. Swartz. That is one thing we would have to determine by experiment.

R. I. Jaffee.*—Is it true that the orientation texture in the columnar crystals is normal to the basal plane?

G. Edmunds.—It is. The basal planes are parallel to the columnar grain axes.

R. I. Jaffee.—It seems to me, since the basal planes are parallel to the surface of the casting, it might be possible to consider that you have columnar crystals at the surface and that any solidification starting from a cooler part would tend to be propagated in the direction perpendicular to the basal planes, whether it is air or iron. In other words, columnar crystals are being propagated from the surface.

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G. Edmunds.—That is a difficult thing to determine. When one takes a metallographic section through a casting and finds a columnar grain, one wonders where that particular columnar grain started. Did it start at the surface or in from the surface a ways? I have taken a number of castings and very carefully metallographic polished them, and have not come to a definite conclusion as to whether the columnar grains stemmed from the surface or began farther in the casting. If you will read the earlier paper,[1] you will find that in zinc we usually have three types of orientation: at the surface the crystals have the basal planes parallel to the surface; in the columnar grains the basal plane (and the crystallographic direction [210]) is perpendicular to the casting surface; and intermediate between the surface and the columnar grains there is frequently an orientation such that the pyramid planes (101) are parallel to the casting surface. These are the predominant orientations at the various depths. Just where the columnar grains start is indefinite. Some seem to start at the surface, but I think most of them start within the casting.

C. E. Swartz.—Why do you think that?

G. Edmunds.—From metallographic examinations in which you can follow to the point of a columnar grain. The beginning of a grain is, of course, a point, and proceeding away from the casting surface the grain enlarges, then becomes of approximately constant cross section, being forced to do so by the presence of other columnar grains. In the metallographic work we followed down to the point of some of the grains. One out of 70 columnar grains examined was found to extend to the cooling surface. Several were found to extend from the cooling surface inward for a distance of approximately ⅛ inch. You realize the difficulty involved in successively polishing and trying to determine the point of a grain.

C. E. Swartz.—I would suggest microradiography for following those down. We have had some very phenomenal success with that in similar studies recently.

I should like also to ask this question: Is it possible for the columnar crystal to be continuous and the orientation of the planes change as the dendrite grows?

G. Edmunds.—It can change slightly. As a matter of fact, the only crystals that I have ever examined have been multiple crystals. The individual cells are lineages that go up with very, very slightly different orientation.

C. E. Swartz.—What I meant was this: As I understand it, most single crystals are really not single crystals in the true sense of the word, but is it possible to have a greater change of orientation than is in the single crystal in the ordinary commercial dendrite that occurs in every-day casting?

G. Edmunds.—I do not believe I can answer positively. I have seen considerable change of orientation even along the length of so-called single crystals. The orientation change was continuous. Several years ago Hoyem and Tyndall[2] reported a similar finding. In fact, they gave conditions under which one could grow crystals that would be of continuous orientation and those that would have a smoothly changing orientation. I do not see that it would make any difference whether it was a columnar grain or a single crystal that was being grown.

C. E. Swartz.—Probably not. I do not know anything about zinc, but it is possible in casting other metal alloys to get what is known to the less theoretical metallurgists as equiaxed dendrite. In other words, you pour a cast metal into a mold and the initial crystallization is a very thin skin of perhaps very short dendrites; then you get this discontinuity, that may be the thing you speak of, and then some long dendrites, which may be a number of inches long in some instances and less in others. Then toward the center are a number of structural shapes, which look somewhat like ordinary equiaxed grains. Whether those are broken up dendrites or not, I never could explain to my own satisfaction how such a thing as that could be formed unless it is a broken dendrite, but some of my friends seem to think they are separate equiaxed dendrites.

Now my question is: If it is an equiaxed dendrite, what would be the orientation of the surface of that particular structural element and what would be the orientation of the interior of that structural element? Would you have the same thing there as in the phenomena you have been describing in your papers?

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[2] A. G. Hoyem and E. P. T. Tyndall: *Phys. Rev.* (1929) 33, 81–89.

G. Edmunds.—I am going to talk first about something a little different from your question. At the Institute of Metals Division meeting last February, some one reported growth of a casting in which from the mold surface upward there were fine grains and then a region of columnar grains and then fine grains and then another region of columnar grains, a thing we had observed several years ago in an attempt to grow a large single crystal of zinc from a rather highly leaded zinc alloy. Of course, we could explain it to our satisfaction by considering that the columnar grain growth proceeded until lead had been pushed ahead of the solidified metal (that amount of lead being insoluble in the zinc), fine grains then formed, entrapping the excess lead, and the process just repeated over and over again.

Now if I understand your other question about equiaxed dendrites, I believe you mean: Will a grain with a dendritic structure be of uniform orientation throughout? In our experience, it will not be.

C. E. Swartz.—Yes.

G. Edmunds.—Precisely of uniform orientation? Shrinkage strains between the dendritic branches mechanically strain them, causing them to be slightly deflected. However, in general it is a uniform orientation, unless you want to get down to fine points.

P. A. Beck.—I believe Campbell and Stead reported in the early 1900's about arsenic-tin-antimony alloys with crystals of a very crooked nature. They found crystals of almost spherical curvature. I suppose, although there is no proof for this, that in this particular case the orientation has undergone very considerable change, as much perhaps as 90° or more within one crystal in a relatively short distance. I suppose composition changes may have accompanied the curvature. I do not know of any other case of so greatly changing orientation in undeformed metallic crystals.

G. Edmunds.—We have run across a number of changes in crystal orientation in specimens thought to be single crystals. We had one beautiful example, a rod about 1½ in. in diameter and one foot long, single crystal of zinc for about 8 in., and then suddenly it went into a very different orientation. We were inclined to feel there might have been mechanical damage of the already formed crystal, and it was a case of strain-anneal growth of a secondary orientation. We have no proof of that.

P. A. Beck.—In that case, you would not call it a single crystal.

G. Edmunds.—That was a bicrystal. I believe a case like the one you mentioned is cited by Hoyem and Tyndall.

Member.—Do you suppose that growth was initially in the final orientation and had by some deformation twisted the surface?

G. Edmunds.—That is a possibility. If local extension near the surface (where the basal planes are parallel to the surface) is visualized, a twinning reorientation of about 94° could occur. The twinned material could then have the orientation observed in the columnar grains. This could then furnish the nuclei for the columnar grains, and these would grow to the exclusion of others, according to the extension of the rule of Bravais.[1]

Member.—Why do you get orientation on the surface? Suppose the orientation on the interior is the initial one growing from the surface and the surface texture was formed by twinning of that original texture.

G. Edmunds.—Why should there be a preferred orientation at the surface? None of the grains have grown any distance; therefore, there has been no selection of nuclei of common orientation. Perhaps an explanation can be derived by considering that growth takes place from points (nuclei) near the surface, and that growth follows the Bravais rule; i.e., as plates perpendicular to the hexagonal axis. Then the area of the surface covered by a plate will be larger, the more nearly it lies parallel to the surface. If the orientation of the nuclei is random, the number of crystals of any one orientation at the surface will be the same as of any other orientation, but the area of surface covered by crystals oriented with basal planes near parallelism with the surface will be enormously larger than the area covered by crystals having basal planes at large angles to the surface. The result will be the surface texture that has been described; namely, basal planes (001) parallel to the surface.

Since nuclei farther from the surface (behind the platelike crystals) may be the sources of new grains of any orientation, including that of the columnar grains, this line of reasoning also rationalizes the origin of columnar grains within the body of the casting. Does any one see an objection to this explanation?

C. E. SWARTZ.—I just had the thought that might help in further work. I thought somewhere in your zinc-recrystallization furnaces there might be some place where the zinc has condensed so slowly that you will find crystals have been produced from areas completely strain-free, perhaps because the zinc is so close to the molten, yet being formed almost from the vapor state, so you might find something there in the as-cast section. If you take a sample of large crystals formed, I imagaine they would be large because they would be formed so slowly.

G. EDMUNDS.—Many grains of zinc have been grown from the vapor phase. They are beautiful crystals with mirror surfaces. We have determined the orientations on some of these; they did not have the same orientation as zinc frozen from a melt.

R. L. SEABURY.*—I am led to believe that the phenomenon you talk about is an interfacial one, whether against air or iron or any other mold surface, and it would appear that it must prefer to solidify in the direction you speak of. In other words, it is going to require energy from some source to tip them up some other way.

Another question: Suppose you turn the casting or otherwise remove this surface, so that you have reached the ends of the columnar crystals and then with a torch or flame bring it up just to the molten point. Next remove the source of heat, and on solidification will it be guided by the columnar crystals below? Possibly going at the thing backward might bring out an explanation.

G. EDMUNDS.—Were we to do that, the solidification would proceed by cooling from the casting outward to the surface. It would be like the case that we mentioned in which there was a heater over the top of the casting and the heat was being abstracted through the casting toward that molten surface.

This discussion has been enlightening and it pleases me immensely that we seem to have reached a rational explanation for the origin of the surface texture—a problem that has been a baffling one for several years.

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Internal Friction of Single Crystals of Brass, Copper and Aluminum

By George H. Found,* Junior Member A.I.M.E.

(New York Meeting, February 1945)

During recent years considerable interest has been focused on the energy-absorption characteristics of metal when it is cyclically stressed in vibration. The most familiar manifestation of this phenomenon, which is called the "damping capacity" or "internal friction" of a material, is involved in the dissipation of mechanical energy of vibration, which otherwise would build up to stress levels where the problems of noise and fatigue are involved.

In addition to its engineering importance in structures, the damping behavior of metals, particularly at low stress amplitudes, has also been used as a unique metallurgical research tool with which to provide sensitive means for indicating certain structural changes within metals. Important contributions toward understanding the energy-dissipating mechanisms that are responsible for internal friction in metals have been made in the last few years. The information is not yet sufficiently extensive, however, to provide a useful metallurgical concept describing exactly how the structure affects the internal friction, or to encourage more general use of this technique among metallurgists.

Three fundamental mechanisms have been proposed, as a result of recent experimental investigations, to account for the internal friction in nonferrous metals in low-stress amplitude tests. These include damping due to internal thermal currents that are created and flow in metal because of differential vibratory stress effects,[1] damping due to localized inelastic stress relaxation at inhomogeneities within the metal,[2,3] and damping related to plastic flow of a localized type for which an explanation has been sought in terms of the dislocation theory.[4] How each of these mechanisms functions as a result of structural changes in the metal is, in general, not well understood because of insufficient experimental data for which the controlling variables have been segregated and because of uncertainties in regard to the nature of the structural changes themselves.

In several investigations the effects of cold-working on the internal friction of polycrystalline brass and aluminum have been described. As reported by Köster and Rosenthal,[5] and by Förster and Breitfield,[6] there is an initial large increase in the damping when the metal is worked. The initial high value is not stable, but declines rapidly, at first, in a hyperbolic manner. About 100 hr. after straining, a stable value is reached of magnitude proportional to the amount of strain.[7] In Fig. 1 is shown the relationship found by Zener and his collaborators between the internal friction due to cold-working of alpha brass and the amount of cold-working.[8]

Several investigators have made internal-friction measurements on worked poly-

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[1] References are at the end of the paper.

crystalline brass after various annealing treatments.[5,8–10] These measurements show that there is a rapid reduction in damping as a result of annealing at temperatures below the recrystallization temperature. Curves obtained by Köster and Rosenthal, (Fig. 2), show that this drop starts in the neighborhood of the recovery-hardening effect found in heavily worked brass. If grain-growth effects are not encountered, the values after annealing equal the values obtained in the brass before straining. Resistivity measurements and X-ray diffraction observations made by Norton after the annealing of alpha brass showed that a complete drop in the damping precedes any other detectable property or structural change. The general conclusion that internal stresses, rather than fragmentation or grain size, are important factors in the internal friction of cold-worked metals has been reached by Köster and Rosenthal and by Norton.

Some information regarding the effect of stressing on the internal friction of copper and zinc single crystals has been published by Read.[4] He observed room-temperature recovery of the internal friction in zinc crystals, but found no analogous effect in copper crystals unless they were annealed at 500°C. When compressive stresses as low as 60 lb. per sq. in. were applied to copper crystals, the internal friction increased greatly. The stress associated with the testing vibrations was sufficient to produce an increase in the internal friction of the zinc crystals. These results together with a dependence on crystallographic orientation of the internal friction for the zinc crystals, which was not observed for copper crystals, were explained by Read in terms of the dislocation theory of slip.

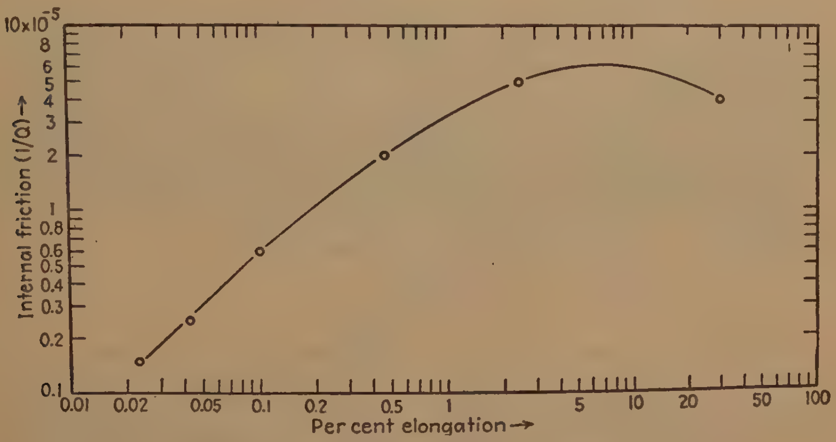

FIG. 1—RELATION BETWEEN INTERNAL FRICTION AND COLD WORKING IN POLYCRYSTALLINE BRASS 16 DAYS AFTER STRAINING. (*After Zener, Clark and Smith.*[8])

The present investigation is concerned with the internal friction of single crystals of aluminum, brass and copper. Measurements were made on the crystals, as cast and annealed, on the crystals after they were stressed below the yield point, after they were cold-worked and after subsequent annealing treatments. The experimental data thus supplied for the single crystals are intended to be analogous to the data obtained for polycrystalline brass. It is interesting to note that the proposed mechanisms that account for the internal friction in metals depend on the existence of inhomogeneities of various type in the metal structure. The elimination of one type of inhomogeneity, due to grain boundaries and the effects of the random orientations of individual grains, may be held responsible for the differences in the results between single and polycrystalline metal that were actually found. The effects of quenching and of alternate slip on more than one family of slip planes (double slip) on the internal friction of single crystals were determined. Measurements of the internal friction of annealed and strained specimens of brass that contained limited grain-boundary areas were also made. These specimens consisted of two or three large grains.

In addition to providing information about the internal-friction characteristics of single and multiple crystalline specimens after various treatments, this investigation was conducted to further demonstrate the use of damping measurements as a research tool for fundamental metallurgical studies.

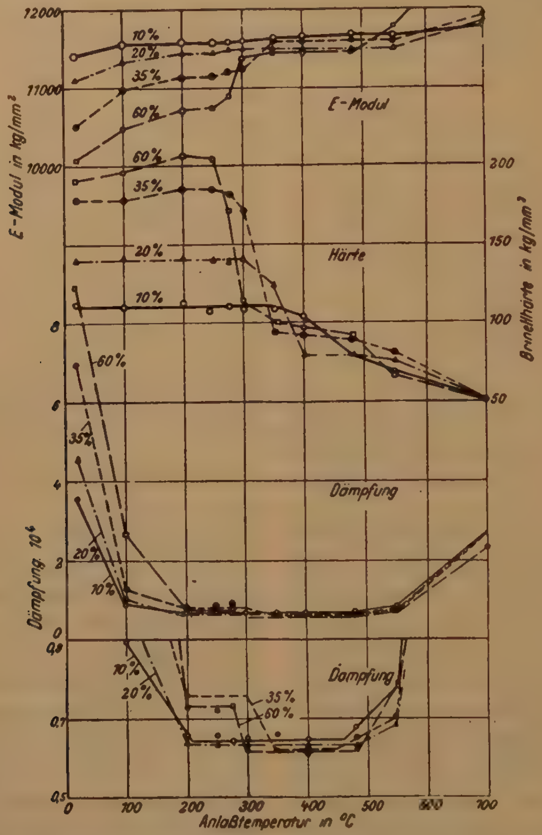

FIG. 2.—INTERNAL FRICTION, HARDNESS AND ELASTIC MODULUS AS A FUNCTION OF ANNEALING TEMPERATURE IN COLD DRAWN POLYCRYSTALLINE BRASS. (*After Köster and Rosenthal.*[5])

EXPERIMENTAL PROCEDURE

The method used for measuring the internal friction was essentially the same as that used by Zener.[10] Both the excitation and detection of the vibrations were accomplished by an electromagnetic coupling between each end of the specimen and the testing apparatus. Cylindrical rod-shaped specimens were supported at the central node of vibration on two horizontal silk threads spaced about ¼ in. apart. The extremities of each test specimen protruded into small, well-shielded solenoid coils. Excitation took place in one coil, which was energized by a stable, frequency-calibrated oscillator. The second coil served as a pickup coil in the detection circuit, which also included an amplifier, oscillograph, and vacuum-tube voltmeter (Fig. 3). All measurements were made in vacuo at room temperature (22 ± 2°C.).

Since the internal-friction values associated with single crystals are generally low, the free decay method for measuring was used, in which long, relatively easily measured time intervals for decay are involved. The internal friction is expressed in terms of a Q^{-1} value. This is $\frac{1}{\pi}$ times the logarithmic decrement ∂ or $\frac{1}{2\pi}$ times the specific damping capacity P; viz.,

$$Q^{-1} = \frac{\partial}{\pi} = \frac{P}{2\pi} = \frac{\ln n}{\pi \tau f}$$

where n is the ratio of the decaying amplitude before to the amplitude after a given time interval, τ. The frequency of vibration, f, was the natural resonant frequency for longitudinal vibration of each specimen measured on the oscillator scale. This frequency ranged from 5550 to 12,600 cycles per sec., depending upon the dimensions, crystallographic orientation, composition, and structural condition of the specimens. The successive amplitudes from which n was determined were measured on a calibrated oscillograph screen after each electrically timed interval. An average was determined from successive values taken along each decay curve. Values were considered only when the decay curve was a true logarithmic time function. Departures from this resulted when the ends of the specimens were fouled with parts of the exciting or detecting units. All amplitudes of vibration used were sufficiently low to render the measurements independent of amplitude and duration of vibration.

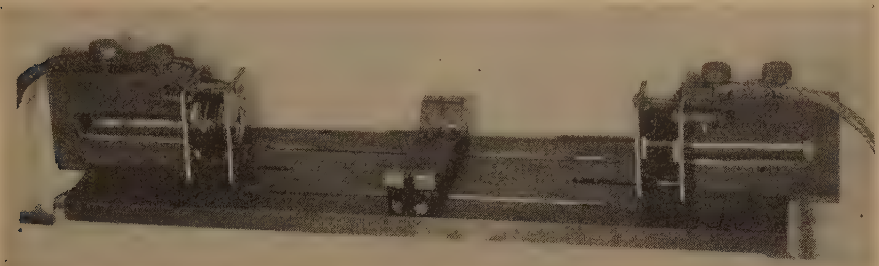

FIG. 3.—PARTIALLY DISMANTLED MOUNTING ASSEMBLY SHOWING EXCITATION AND DETECTION UNITS.

Single-crystal specimens of brass, copper, and aluminum were made by the Bridgman method of gradual solidification. The details of the technique as conducted in the Hammond Laboratory may be found elsewhere.[11–13] The crystals were cast about ⅝ in. in diameter and 8 to 10 in. long. The copper and several of the brass single crystals were made for previous single-crystal studies in the Hammond Laboratory by other investigators.

The composition of the original metal and other data pertinent to the production of the single crystals are itemized in Table 1. An objectionable factor in making the brass single crystals was the unavoidable loss of zinc by evaporation from the molten surface during the solidification process, in spite of the liberal use of a flux cover. Chemical analyses of several brass single crystals made by Burghoff under conditions similar to those employed here showed the zinc loss to be about one per cent.[14] The bicrystalline and tricrystalline specimens used in this investigation were selected from among the unsuccessful products of the single-crystal process.

TABLE 1.—*Production of Specimens*

Specimen No.	Producer	Method of Production	Original Material
Brass		Brass-borax cover in air environment	½-in. dia. extruded rod of high-grade 70-30 brass. Impurities not in excess of 0.006 per cent Pb, 0.008 per cent Fe, 0.002 per cent Ni
F_1	G. H. Found		
F_2	G. H. Found		
F_3	G. H. Found		
F_4	G. H. Found		
F_6	G. H. Found		
P_1	H. L. Burghoff[14]		
P_2	H. L. Burghoff[14]		
P_4	I. Pickus		
P_7	I. Pickus		
P_8	I. Pickus		
P_9	I. Pickus		
P_{10}	I. Pickus		
P_{12}	I. Pickus		
P_{16}	I. Pickus		
P_{20}	I. Pickus		
Copper		Under oxygen-free nitrogen atmosphere	O.F.H.C. copper, 99.985 per cent pure
Cu_1	W. R. Hibbard, Jr.[12]		
Cu_2	W. R. Hibbard, Jr.[12]		
Cu_3	W. R. Hibbard, Jr.[12]		
Cu_4	W. R. Hibbard, Jr.[12]		
Aluminum.		In air environment	½-in. dia. extruded rod 0.006 per cent Si, 0.015 per cent Cu, 0.004 per cent Fe, 99.975 per cent Al
P_A	G. H. Found		
P_B	G. H. Found		
P_K	G. H. Found		
P_L	G. H. Found		

Before internal-friction measurements were made on any of the crystals, the ends were carefully squared off to promote more efficient energy transfer at the extremities of the test pieces. This was done with the aid of a small cotton-padded miter box and jewelers' saw. The cold-working at the sawed interfaces was then removed by alternate etching and abrasive treatments. Annealing treatments of 3 hr. at 825°C. for all brass and copper specimens, and of 6 hr. at 600°C. for the aluminum specimens, were then given prior to making any internal-friction measurements.

Preliminary internal-friction measurements reported in Table 2 demonstrate the extreme sensitivity of this property in single crystals to handling. Brass specimens F_1 and F_6 were tested shortly after being cast and at intervals of one and four days, between which times the two crystals were carried in a cardboard container from one location to another. Occasionally, the crystals rolled or gently bumped together in transit. The resultant increase is evident. When the specimens were machined into tensile-test shape, a further increase was effected. The net increase in these measurements was eliminated by a 3-hr. anneal at 500°C. The internal friction of a third crystal, F_3, was measured before and after a 14-day interval, during which time the specimen suffered no handling other than that necessary for careful installation in the measuring unit. No change was evident. All subsequent handling was done in cotton-lined boxes without further variations.

TABLE 2.—*Effect of Handling on Internal Friction of Brass Crystals*

Q^{-1} values corrected to 7000 cycles per second

F_1	F_6	F_3
0.65×10^{-5} as cast and annealed	1.74×10^{-5} as cast and annealed	0.57×10^{-5} as cast and annealed
0.91 (1 day later)	1.85 (1 day later)	0 57 (13 days later)
0.96 (4 days later).	2.28 (4 days later)	
1.57 (after machining and etching)	5.10 (after machining and etching)	
0.65 (3 hr. anneal 500°C.)	1.75 (3 hr. anneal 500°C.)	

From previous research on polycrystalline brass and single crystals it is apparent that the internal friction is dependent upon the frequency of vibrations at which the measurements are made.[1,2,4,8] Since it was desired in the course of this investigation to compare internal-friction values of crystals having varying resonant or testing frequencies, it was requisite that the exact relationship between the two variables be found.

Accordingly, internal-friction measurements were made on several different brass specimens and one aluminum specimen at different frequencies in both the annealed and worked condition. The testing frequency was altered between measurements on each crystal by changing the mass of the specimens.

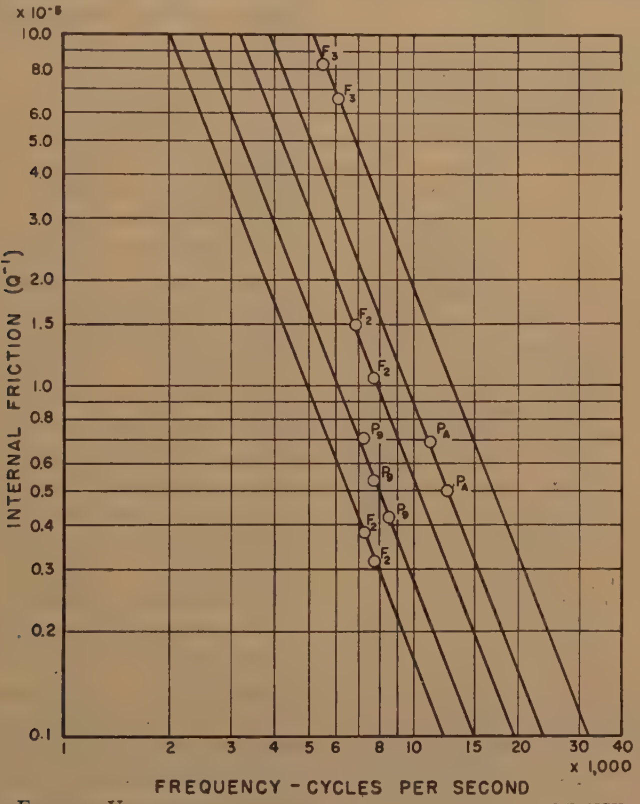

FIG. 4.—VARIATION OF INTERNAL FRICTION WITH FREQUENCY.

P_A is as-cast aluminum.
P_9 is as-cast brass.
F_2 is brass drawn 2 per cent for the higher values and is annealed crystal for lower values.
F_3 is brass measured 2 hours after 16 per cent elongation.

The results are plotted on log-log coordinates in Fig. 4 for specimens P_9, F_2, F_3, and P_A. The internal friction of the annealed specimens at room temperature varies with the frequency in a manner characteristic of the damping that has been associated with internal thermal currents.[2,8] The internal friction attributable to cold-working, which is the difference between the curves for the cold-worked and those for the annealed specimens, is also a function of the frequency of measurement. In polycrystalline metal, the internal friction due to cold-working has been found to be independent of frequency.[8]

Since the desired relationship has been determined, it is quite simple to compare internal-friction measurements on single crystals by converting them to a convenient standard frequency. The standard frequency chosen was 7000 cycles per sec. It must be remembered that as the number of grains in the specimen increases, departures from this linear law are observed. There is no reason to believe, however, that the presence of the limited number of grains in the bicrystalline and tricrystalline specimens would appreciably alter this relationship. It was, therefore, used for these specimens.

RESULTS ON BRASS CRYSTALS

The crystallographic orientation as determined from Laue X-ray photograms of each of 15 brass crystals is shown in the stereographic plot in Fig. 5. The axis of each specimen with respect to the basic stereographic triangle is indicated by each point.

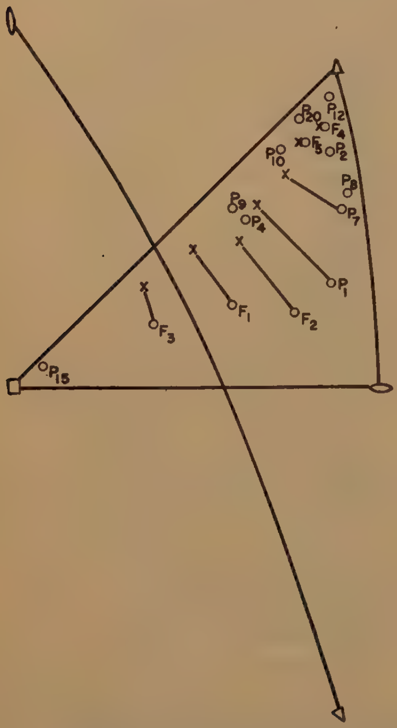

FIG 5.—STEREOGRAPHIC PROJECTION SHOWING CRYSTALLOGRAPHIC ORIENTATION OF BRASS CRYSTALS.
Migration of axes of strained crystals is shown.

The internal-friction values of these 15 crystals as cast and well annealed were measured and plotted against the frequency for each crystal (Fig. 6). When the measurements are corrected to the standard 7000 cycles per sec., the values assume the relative positions shown in Figs. 7 and 8. The values are grouped with definite relation to the crystallographic orientation of the specimens. The values for specimens F_4, F_5, P_{10}, P_{12}, and P_{20}, whose poles are all in the proximity of the octahedral or (111) pole, are at a maximum, while the crystals whose poles are oriented in the proximity of the cubic or (100) pole, exhibit the lowest values of internal friction. Thus, from the disposition of the values in Fig. 8, it is apparent that there is an orientation dependence of the internal friction in single crystals of brass.

Seven of the 15 previously tested brass single crystals were prepared for straining in tension. A reduced section was prepared on each of the specimens in order to encourage uniform straining and to confine the damage to the metal structure done by the testing grips to limited regions in the extremities of the specimens. The brass and aluminum crystals were carefully machined into the cylindrical tensile-test shape. Successive light cuts of several thousandths of an inch were removed with each pass. The cold-working on the surface was then removed by alternate abrasion and etching treatments. The copper crystals were too ductile to be machined, so were prepared by the abrasion and etching technique alone. During all etching treatments the grip sections of each specimen were protected with picein wax. These grip sections were ⅝-in. long. The final diameter of the reduced section of all specimens was between 0.455 and 0.508 in. and was constant throughout the reduced section to ±0.0008 inch.

No differences were observed between the Laue X-ray spots in photograms taken before and after the preparation of the tensile specimens. The internal-friction values resulting from the machining of specimens F_1 and F_5 changed slightly as shown in Table 2 and, as already mentioned, were restored to their initial values by a 3-hr. anneal at 500°C. All specimens were therefore well annealed after machining.

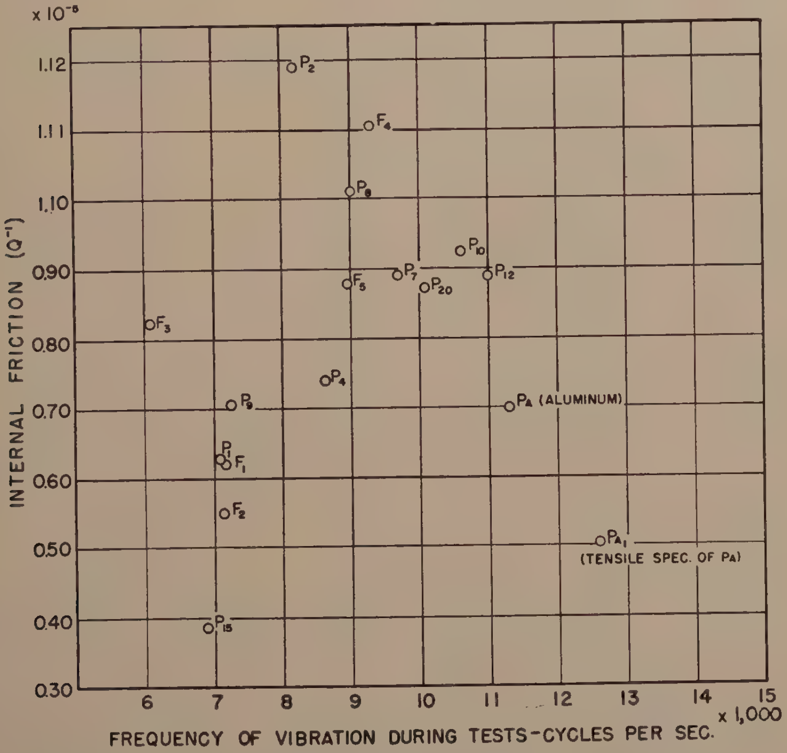

FIG. 6.—INTERNAL FRICTION OF AS-CAST AND ANNEALED CRYSTALS PLOTTED AGAINST MEASURED FREQUENCY OF VIBRATION.

Preliminary internal-friction measurements were made on single-crystal specimens with the ⅜-in. grip sections attached and with the sections removed. After correcting for the frequency change effected by the change in mass, no variation in the measurements due to the presence of the grip sections was observed, even in the most heavily strained specimens. The probable reason for the insensitivity of the internal-friction measurements to the structural condition within the grip sections is that, owing to the depth of protrusion into the coils, the vibrations originated and were detected within the diminished gauge length of the specimens, thus rendering unimportant the transit of the vibrations through uncertain grip sections. Therefore, when more than one straining was given a specimen, the grip sections were not removed, but in all other cases they were removed, to eliminate a possible influence during recrystallization treatments.

Specimens F_1, F_2, and F_3 were stressed in tension to various amounts below their respective yield points as shown in Table 3. The yield points were calculated by crystallographic methods based on the published value for the critical resolved shear stress for this brass of 1990 lb. per sq. in.[13] The yield points determined from the stress-strain curves plotted for the measured extensions were in close agreement with the calculated values. In no case was there an appreciable increase in the internal friction. In fact, in F_1 and F_3 the internal friction decreased after loads as high as 700 lb. were applied. A microscopic examination revealed no evidence of plastic deformation. Specimen F_2 was subsequently strained just to the yield point. Abruptly the internal friction increased, and eight grouped glide ellipses appeared in different portions of the specimens, thus apparently confirming the results of other investigators that brass single crystals have well-defined yield points. Specimen F_1 was given a 0.065 per cent strain. An increase in the internal friction greater than 250 per cent resulted. An elongation of 11 per cent in F_3 also resulted in a drastic increase.

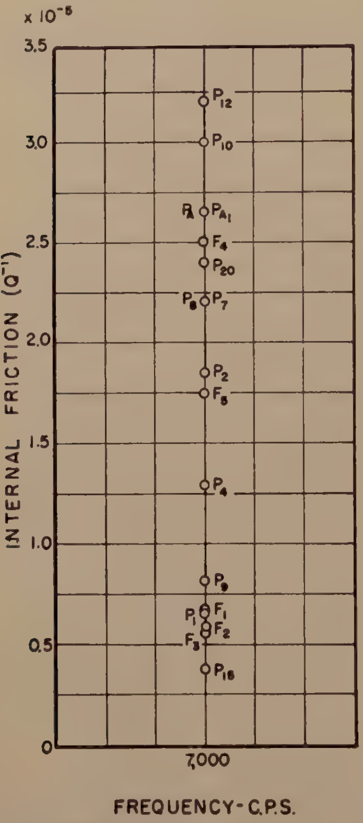

FIG. 7.—INTERNAL FRICTION VALUES CORRECTED TO 7,000 C.P.S.

It was desired to obtain a correlation between different amounts of cold-work and the internal friction for single crystals of brass and to compare this with a similar correlation that Zener obtained for polycrystalline specimens. Seven brass single crystals F_1, F_2, F_3, F_4, F_5, P_1 and P_7, were strained to various amounts. The migration of axes of the strained crystals is shown in Fig. 5.

TABLE 3.—*Effect of Stressing Brass Crystals*[a]

F_1	F_2	F_3
0.65 × 10^{-5} as cast and annealed	0.57 × 10^{-5} as cast and annealed	0.57 × 10^{-5} as cast and annealed
0.48 350 lb. load (1880 lb. per sq. in.)	0.64 350 lb. load (2050 lb. per sq. in.	0.53 700 lb. load (3800 lb. per sq. in.)
1.24 1 hr. after strained 0.065 per cent (yield point exceeded)	0.60 580 lb. load (3420 lb. per sq. in.)	9.0 1 hr. after strained 11 per cent (yield point ex ceeded)
	0.76 725 lb. load (4260 lb. per sq. in.) (yield point exceeded)	
	5.0 1 hr. after strained 2 per cent (yield point exceeded)	

[a] All Q^{-1} values quoted in this and subsequent tables are corrected to 7000 cycles per second.

Internal-friction measurements were made on strained specimens at intervals of time approaching 400 hr., as shown in Fig. 9. These reveal a condition of instability that has been previously observed for both polycrystalline metal and single crystals of zinc. The values decreased with time from magnitudes dependent upon the amount of shear strain to the proximity of the value for the original unstrained specimens. The relative magnitudes of the values 400 hr. after straining were not related to their strain histories. The extent of the decline appears to be considerably greater than in the values for strained polycrystalline brass and other polycrystalline metals.

The general relationship, degree of cold-working vs. internal friction, could be best expressed in terms of the shear strain vs. Q^{-1} value as shown in Fig. 10. The nonuniform nature of the decaying tendency necessitated that values be chosen early in the decay. The values were therefore taken from the curves in Fig. 9 one hour after straining.

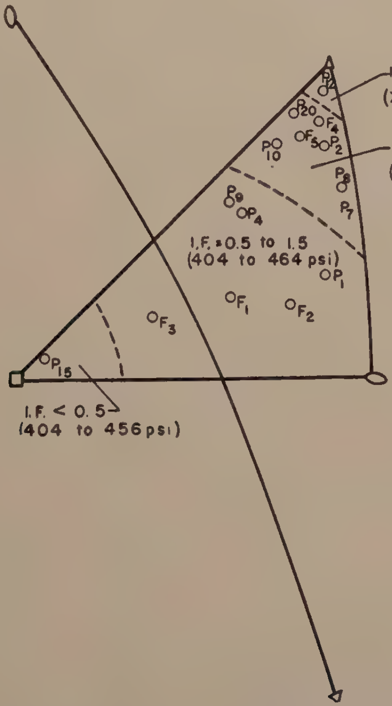

FIG 8.—ORIENTATION DEPENDENCE OF INTERNAL FRICTION OF BRASS SINGLE CRYSTALS SHOWN IN A STEREOGRAPHIC TRIANGLE TOGETHER WITH CORRESPONDING, CALCULATED, MAXIMUM AND MINIMUM YIELD STRENGTHS FOR THE CRYSTALS IN EACH REGION.

Annealing treatments were given several of the strained specimens in the course of their internal-friction decline. The results are summarized in Table 4.

A 50°C. anneal for 2 hr. had no detectable effect on F_4. A 100°C. anneal for 2 hr. accelerated the decline appreciably in F_4 and, after 15 hr., decreased the Q^{-1} value for F_3 to about 40 per cent below its as-cast value. A 500°C. anneal for 3 hr. on F_2 accelerated the Q^{-1} decline to a value 26 per cent below the as-cast value. An 825°C. anneal on F_1, which had been

TABLE 4.—*Effect of Annealing Deformed Brass Crystals*

Specimen No.	Q^{-1} As Cast and Annealed	Shear Strain	Q^{-1} Before Anneal	Anneal Treatment		Q^{-1} After Anneal
				Hr.	Deg. C.	
F_4	2.45×10^{-5}	0.055 (2 per cent elongation)	5.5×10^{-5}	2	50	5.5×10^{-5}
F_4	2.45	0.055	4.9	2	100	4.0
F_4	2.45	0.055	3.15	3	825	3.85[a]
F_3	0.57	0.24 (11 per cent elongation)	3.6	15	100	0.35
F_3	0.57	0.24	0.35	1½	825	1.1[a]
F_2	0.57	0.043 (2 per cent elongation)	1.39	3	500	0.42
F_1	0.65	0.012 (0.065 per cent elongation)	0.80	3	825	0.60
F_5	1.75	0.05 (2 per cent elongation)	1.84	½	825	2.30[a]

[a] Recrystallized.

only lightly strained, also resulted in a lowering of the Q^{-1} value below that for the initial as-cast state. In more severely strained specimens, however, recrystallization resulted during the 825°C. anneal with an accompanying increase in the Q^{-1} value. In specimens whose internal friction had been previously decreased by 100°C. and 500°C. treatments (F_4, F_3, and F_2), the values abruptly increased when recrystallization took place at 825°C., owing to the introduction of grain boundaries and nonuniform orientation into the specimens. Two specimens with similar orientations, F_1 and F_2, after the annealing treatments in Table 4 were strained to 20 per cent elongation. Specimen F_2 was annealed 1½ hr. at 825°C., 3½ hr. after straining, while F_1 was annealed under identical conditions 410 hr. later. In spite of the fact that the internal friction of the latter had decreased to 0.91×10^{-5} before annealing, both exhibited equally profuse recrystallization.

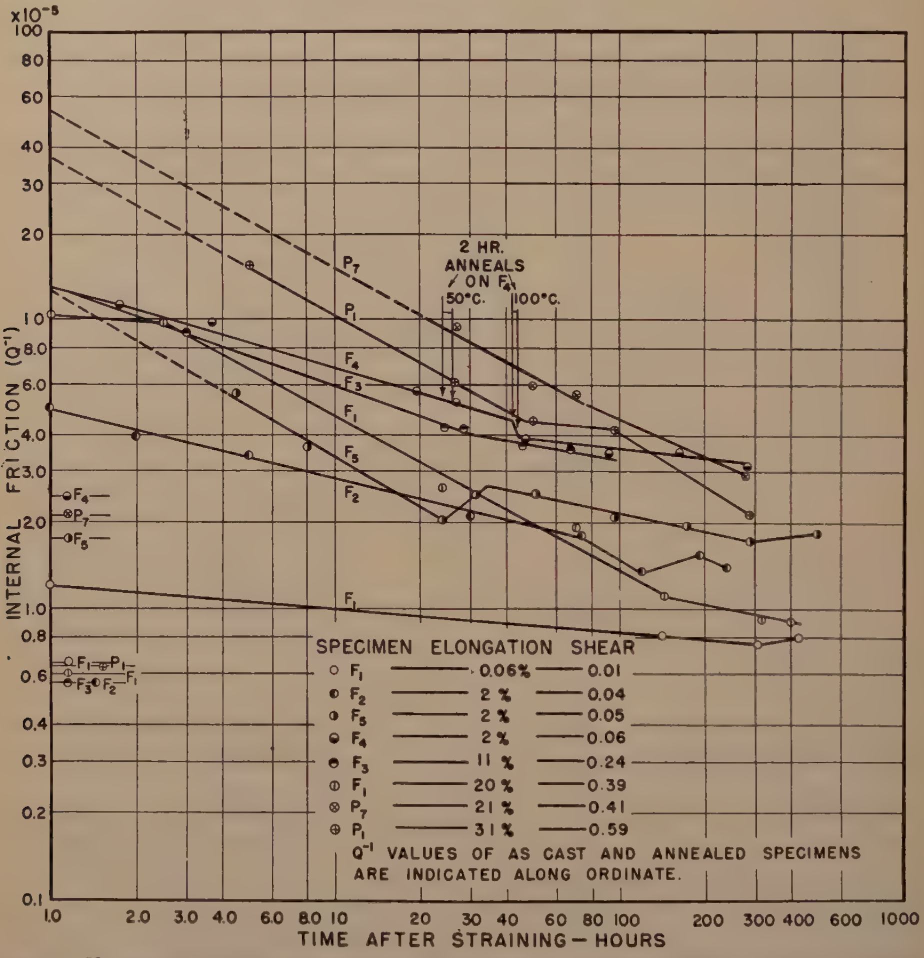

FIG. 9.—VARIATION OF INTERNAL FRICTION WITH TIME IN STRAINED SINGLE CRYSTALS OF BRASS.

The occurrence of double slip, or slip alternately on each of two families of operative glide planes, was investigated. Specimen P_{12} of Table 5 was strained to 4 per cent elongation. Secondary slip markings became very irregularly spaced because the specimen had to submit to the conflicting influences of two operative slip systems. Not until 53 hr. after the straining was the internal friction down within the range measurable on the equipment; that is, less than 50×10^{-5}. A stable value, which was considerably above the as-cast value, was reached 222 hr. after straining.

TABLE 5.—*Effect of Double Slip*

P_{12}	
3.1×10^{-5}....	As cast and annealed
25............	53 hr. after strained to 4 per cent elongation
7.3...........	222 hr. after straining
7.3...........	312 hr. after straining

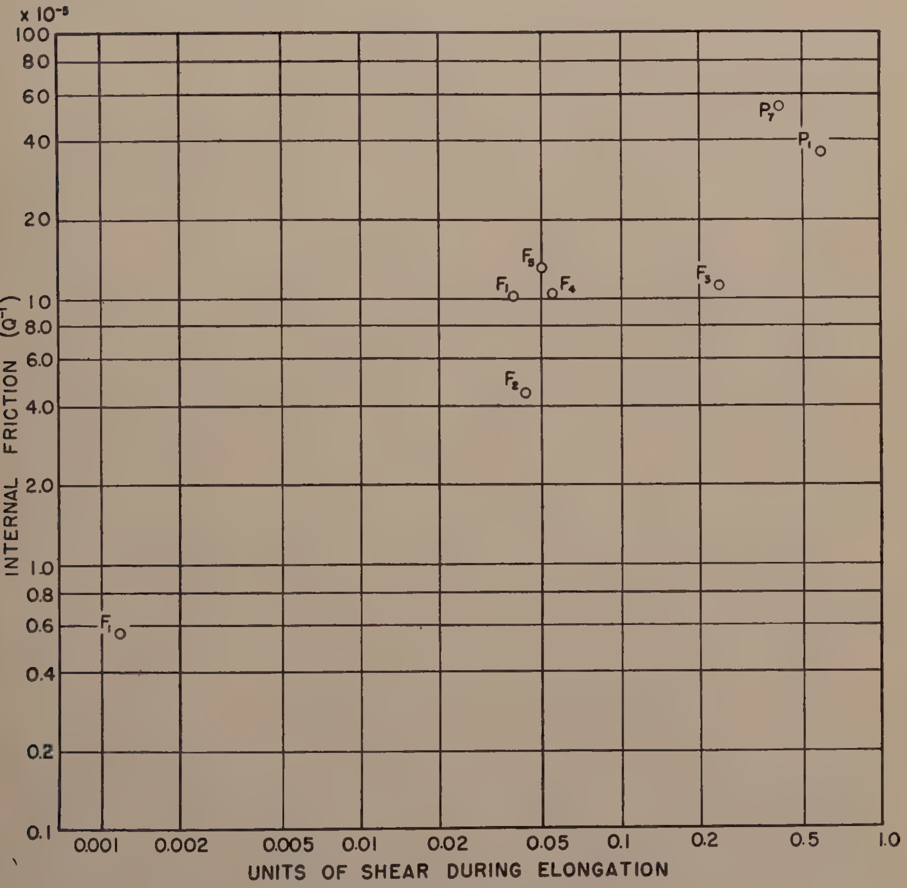

FIG 10.—RELATION BETWEEN INTERNAL FRICTION DUE TO COLD WORK AND SHEAR IN STRAINED BRASS SINGLE CRYSTALS.
One hour after straining.

The internal-friction effects accompanying the compressive stressing of a brass single crystal are similar to those for loads applied in tension. Specimen P_8 was cut down to a cylindrical shape 6 in. long and about 0.455 in. in diameter. The ends were carefully squared off so that axial loading would be possible. Stressing below the compressive yield point caused the internal friction to decrease as shown in

Table 6. When the compressive yield was exceeded, the Q^{-1} value increased. Read has demonstrated that stresses as low as 60 lb. per sq. in. effected very large increases in the internal friction of copper crystals.

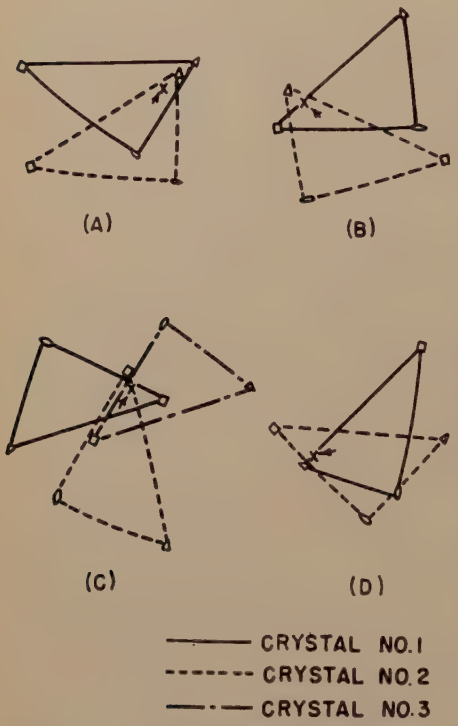

FIG. 11.—SUPERIMPOSED STEREOGRAPHIC DIAGRAMS SHOWING RELATIVE ORIENTATIONS OF GRAINS IN THE BI- AND TRI-CRYSTALLINE SPECIMENS.

Axes of specimens are at arrows. (A) = B_{I}, (B) = B_{II}, (C) = B_{III}, (D) = B_{IV}.

TABLE 6.—*Effect of Compression*

P_8	
4.2×10^{-5}	As cast and annealed
3.8	100 lb. load (620 lb. per sq. in.)
3.5	300 lb. load (1860 lb. per sq. in.)
7.4	500 lb. load (3100 lb. per sq. in.) (yield point exceeded)

Brass specimen P_4 was heated to 530°C. and quenched by complete immersion in water. Twenty minutes after the quench the Q^{-1} value was 250 per cent higher than in the initial annealed state, and 55 min. after quenching it was about 10 per cent above the original as shown in Table 7. A second specimen P_{10} was heated to 825°C. and quenched from each end by jets of water. It was thought that the large stress gradients in the ends of the specimens might have a pronounced effect on the internal friction. The increase in Q^{-1} value, however, was less and was relieved more rapidly than for specimen P_4. The influence of the quenching on the factors that determine the internal friction in single crystals is small and evidently quickly relieved.

TABLE 7.—*Effects of Quenching Single Crystals*

P_4		P_{10}	
1.30×10^{-5}	As cast and annealed	3.0×10^{-5}	As cast and annealed
3.2	20 min. after quench from 530°C.	3.6	20 min. after ends were quenched from 825°C.
2.1	25 min. after quench	3.2	30 min. after quench
1.4	55 min. after quench		

RESULTS ON BICRYSTALLINE AND TRICRYSTALLINE BRASS SPECIMENS

Studies were made on specimens having limited grain-boundary regions. One tricrystalline and three bicrystalline specimens of brass were prepared for testing and tensile-stressing in the same manner as were the single crystals. The relative orientations of the grains to each other are shown in the superimposed stereographic triangles in Fig. 11.

The internal friction of the specimen in the as-cast and annealed states could not be related to any of the three factors; area of grain boundary in the specimens, orientation of constituent grains or relative orientation of grains. Specimen B_{IV} exhibited the lowest Q^{-1} value, as shown in Table 8. Its grains, however, had very diverse orientations and the area of the grain boundaries was relatively large. The maximum Q^{-1} value was obtained for specimen B_{II}. The orientations in this specimen were also very different and the area of the grain boundaries was relatively small.

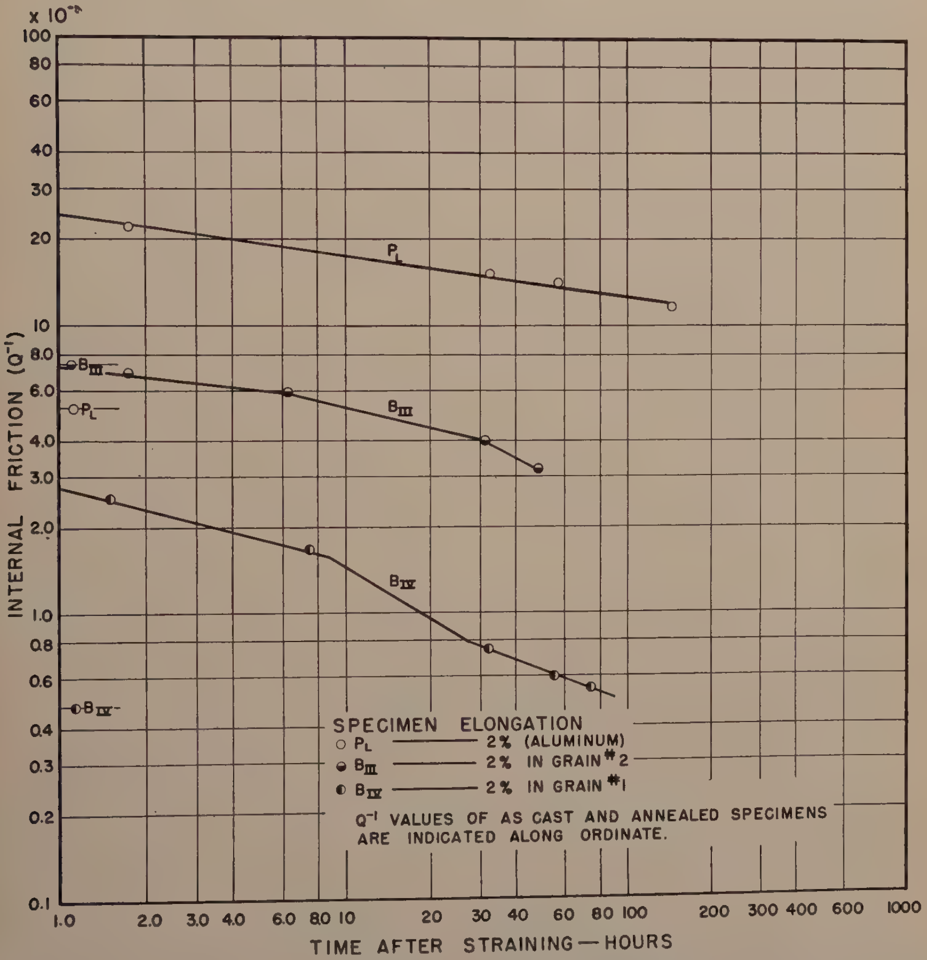

FIG. 12.—VARIATION OF INTERNAL FRICTION WITH TIME IN STRAINED BI- AND TRI-CRYSTALLINE BRASS SPECIMENS AND IN ALUMINUM CRYSTALS.

The application of tensile stress not in excess of the lowest critical resolved shear stress for any of the constituent grains caused large-scale drops in the Q^{-1} values. The decreases were of magnitude approximately proportional to the initial magnitude of the internal friction in the annealed state, and also proportional to the applied stress as long as it was below the yield point. In some cases this decrease exceeded 450 per cent.

Specimens B_{III} and B_{IV} were strained to 2 per cent elongation and B_I and B_{II} to 7 per cent elongation, as measured in the respective grains of highest critical resolved shear stress. The initial magnitude and decline of the Q^{-1} values for B_{III} and B_{IV} are shown in Fig. 12. The values of these strained specimens more rapidly approached a stable value below that for the as-cast state than did those of the single crystals. The value of B_{III} 49 hr. after straining was apparently stable, since a 3-hr. anneal at 100°C. had no effect on the Q^{-1} value.

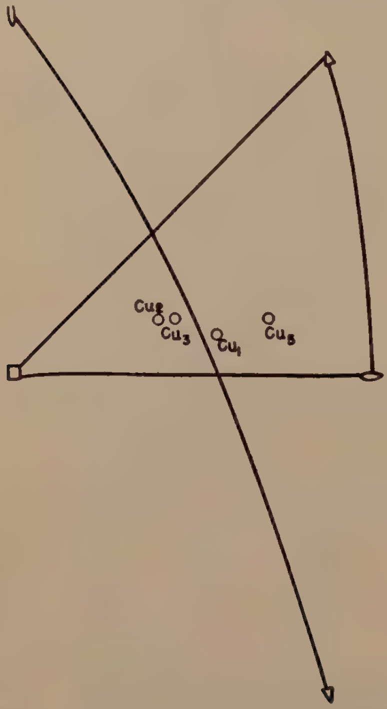

FIG. 13.—STEREOGRAPHIC PROJECTION SHOWING ORIENTATION OF THE COPPER SINGLE CRYSTALS.

TABLE 8.—*Stressing of Multi Crystals*

B_{I}	B_{II}	B_{III}	B_{IV}
As cast and annealed 6.9×10^{-5} 700 lb. load 5.3×10^{-5}	As cast and annealed 11.5×10^{-5} 600 lb. load 5.7×10^{-5}	As cast and annealed 7.4×10^{-5} 600 lb. load 2.65×10^{-5} 1000 lb. load 2.05×10^{-5}	As cast and annealed 0.48×10^{-5} 500 lb. load 0.38×10^{-5}

RESULTS ON COPPER CRYSTALS

The crystallographic orientations of the four copper single crystals that were investigated are shown in Fig. 13. A relationship between the internal friction in the annealed state and the orientation could not be determined on the basis of only four specimens. It was evident from the internal-friction measurements that the copper crystals reacted quite differently to applied stress than did the brass crystals. For tensile stresses applied well below the yield stress, the Q^{-1} value increased as shown in Table 9.

TABLE 9.—*Effect of Stressing Copper Crystals*

Cu_1	Cu_2	Cu_3	Cu_4
As cast and annealed 5.6×10^{-5}	As cast and annealed 1.4×10^{-5} 130 lb. load 5.5×10^{-5} 25 hr. after above loading 3.4×10^{-5}	As cast and annealed 0.96×10^{-5} 100 lb. load 4.4×10^{-5} 26 hr. after above loading 3.9×10^{-5} 49½ hr. after above loading 3.2×10^{-5}	As cast and annealed 3.1×10^{-5} 3 days later 3.1×10^{-5}

With room-temperature aging, these values declined 25 per cent in 50 hr. Tension loads exceeding the yield stress caused an increase in the internal friction beyond the range of the testing apparatus. After 500 hr. the values were still out of range. A 3-hr. anneal at 100°C. had no measurable effect.

RESULTS ON ALUMINUM CRYSTALS

The crystallographic orientations of the four aluminum single crystals tested are shown in Fig. 14. The unstandardized Q^{-1} values for these crystals in the as-cast and annealed states were of the same order of magnitude as the brass and copper; however, since the resonant frequency of the aluminum was about 30 per cent higher than for the brass or copper, the Q^{-1} values, when corrected to 7000 cycles per sec., were much higher than for the other two metals.

Stressing below the yield point produced the same effect in the aluminum as in the brass crystals. Loads of 100 and 150 lb. on two different crystals effected decreases of 30 and 50 per cent, respectively, as shown in Table 10. After specimen P_L was strained to 2 per cent elongation, the Q^{-1} values subsequently decreased with time (Fig. 12).

DISCUSSION OF RESULTS

Certain aspects of the results from this investigation are not compatible with theoretical explanations advanced in the past to account for internal-friction phenomena.

TABLE 10.—*Effect of Stressing Aluminum Crystals*

P_A	P_B	P_K	P_L
As cast and annealed 2.65×10^{-5}	As cast and annealed 14×10^{-5} 150 lb. load 7.0×10^{-5}	As cast and annealed 10×10^{-5} 100 lb. load 7.0×10^{-5}	As cast and annealed 5.2×10^{-5}

By means of the dislocation theory, Read has related his observations of the internal friction of metals to the mechanism of slip or plastic deformation.[4] According to this theory, dislocations, which are imperfections of a particular type in the crystal lattice and are produced by cold-working, move back and forth under the influence of the applied vibrations. This motion dissipates the applied vibrational energy, thereby causing internal friction. The magnitude of the internal friction is thus directly related to the density of the dislocations in the crystal. According to the dislocation theory, the process of slip in the crystal lattice is carried out by the creation and migration of the dislocations. Since it is known that the slip process is a function of the crystallographic orientation of the lattice, the dislocation theory of internal friction predicts that the internal friction must also bear a similar relation to orientation. Read observed such a relationship in zinc crystals, which have a hexagonal structure, but found none in copper, which has a face-centered cubic structure. This was explained by Read in terms of the dislocation theory and the greater dependence upon orientation of the slip systems in zinc than in copper.

In the present investigation the internal friction of single crystals of brass, which are face-centered cubic, was found to be very definitely a function of orientation. Moreover, the nature of this dependence is not related to the plasticity of the crystals. This is demonstrated in Fig. 8. The highest internal-friction values were measured at orientations where the crystals have their highest resistance to plastic deformation. It is difficult to explain these observations in terms of the dislocation theory in its present state. A factor that may contribute to the difference between the observations of Read and those in the present investigation is the vibrational stress amplitude used for testing. The amplitudes used by Read were higher than those employed here.

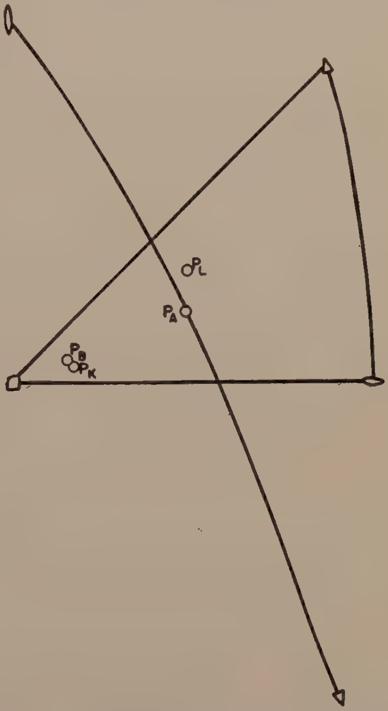

FIG. 14.—STEREOGRAPHIC PROJECTION SHOWING ORIENTATION OF THE ALUMINUM SINGLE CRYSTALS.

Certain investigators have suggested a relation between internal-friction phenomena and internal stresses, particularly for use in explaining low-temperature recovery effects.[5] The apparent independence of the capacity for recrystallization (specimens F_1, F_2, F_3, F_4, and F_5) and the internal friction, as well as the small and transient influence of quenching stresses on the internal friction (specimens P_4 and P_{10}), demonstrate that residual microstresses and macrostresses, respectively, have only a secondary effect on the fundamental agency promoting internal damping at low amplitudes.

Evidence that the internal friction of the annealed single crystals could be due in part to damping of the thermal current type is provided in Figs. 4 and 8. The frequency dependence is in general agreement with observations that previous investigators have interpreted in terms of energy dissipation by internal thermal currents. The nature of the dependence of the damping values upon orientation is also suggestive of thermal current damping in the annealed crystals. The properties of elasticity are closely related to thermal current phenomena. The moduli of elasticity for brass for different crystallographic planes ($E_{(111)}/E_{(100)} = 3.5$) bear a relation to the internal-friction values at similar orientations that is compatible with thermal current damping. An explanation is not available, however, for interpreting in terms of the thermal current theory the recovery effects that are observed in the internal-friction values at room temperature and at low annealing temperature, nor can the internal-friction phenomena associated with small tensile or compressive loadings be satisfactorily explained by this theory.

It is interesting to consider the observed internal-friction measurements in terms of the theory of localized relaxation for damping.[2,3]

Essentially, the relaxation theory, as described by previous investigators, depends upon the presence of certain localized areas within the metal structure that cannot maintain shearing stresses. Shearing stresses thus give rise to local plastic straining, or relaxation. This effects a readjustment of stresses in and adjacent to the relaxation centers. The relaxation centers are associated with inhomogeneities of some type within the structure, such as impurities, slip planes, solute dispersion and grain boundaries. Thus, cold-working, for instance, creates a large number of relaxation centers. Vibratory stresses impressed upon a cold-worked structure will be dissipated at the relaxation centers by local plastic action, thereby resulting in the high internal friction associated with cold-worked metal.

The inability of relaxation centers to maintain shearing stresses equivalent to the nominal strength of the metal has been ascribed to inherent weakness or low creep strength in the localized relaxation centers; thus, the presence of a discontinuous plastic phase in metals has been hypothesized.

This theory of relaxation can be used to explain the internal friction of the stable type such as that found in cold-worked polycrystalline metals[3] or in single crystals at elevated temperature.[2] It is not apparent, however, how this theory can be used to explain the unstable type observed as a result of the stressing treatments in this investigation.

A new theory of localized relaxation must be formulated, which does not involve the existence of a stable discontinuous plastic phase of inherently low shear strength. A type of localized residual stress is postulated that indirectly depends for its existence upon structural inhomogeneities. These localized residual stresses effectively preload areas of eventual relaxation. The allowable shearing stress or vibratory stress that can then be superimposed on the areas of localized residual stress, for any given amount of localized relaxation, is as effectively reduced as it would be in metals containing the hypothetical areas of inherently low shear strength.

Associated with the presence of grain boundaries, even in limited amount (specimens B_{I}, B_{II} and B_{III}), is usually a value of internal friction that is higher than in annealed single crystals. This value of internal friction in the annealed, as-cast, single crystals of brass and aluminum is lowered by stressing the specimens below the yield point, as shown in Tables 3 and 10. This effect is magnified in the bicrystalline and tricrystalline brass specimens. In terms of the relaxation phenomenon, the localized residual stresses, which evidently cannot be completely eradicated by annealing, are redistributed, and thus eliminated, by lightly stressing the metal in tension or compression to loads less than the nominal yield point.

Cold-working has a greater permanent effect upon the internal friction of polycrystalline metal than upon that of single crystals. The internal friction associated with the cold-working in polycrystalline brass is stable after 100 hr. and is proportional to the amount of working. The internal friction associated with cold-working in single crystals of brass is proportional to the amount of working immediately after stressing, but completely disappears with time, as shown in Fig. 9. It can, therefore, be concluded that the localized residual stresses produced by cold-working single crystals of brass redistribute themselves, or recover, at room temperature. This recoverable type of residual stress must be associated with the slip planes, since these are the predominating type of inhomogeneity present in cold-worked single crystals. The localized residual stresses produced by cold-working in polycrystalline brass do not completely recover at room temperature. The unrecoverable type of localized residual stresses must be associated with the grain boundaries and the random orientation of the grains.

Annealing treatments effect an acceleration of the decline in internal-friction values, as indicated by the measurements in Table 4. Such treatments apparently do not completely eliminate the effective residual stresses manifest in the internal-friction measurements unless the single crystals have been previously worked. Sufficient annealing of cold-worked single crystals gave internal-friction values lower than the as-cast and annealed values, providing recrystallization did not take place.

The development of localized residual stresses must take place at much lower applied stresses in copper than in brass or aluminum single crystals. This is indicated by the large increases in the internal friction accompanying the stressing of copper crystals far below their respective yield points. Such effects do not take place in brass and aluminum crystals until their yield points are exceeded.

An interesting interpretation of the recovery-hardening portion of the annealing curve is possible in terms of the relaxation theory presented. It will be noted in Fig. 2 that the drop in internal friction appears to coincide with the recovery-hardening effect observed for the most heavily worked brass specimens. The internal-friction measurements indicate that a redistribution or recovery in the localized residual stresses takes place in the region of the annealing curve where the internal friction decreases. This implies that the presence of these stresses in heavily worked polycrystalline brass is manifest as detrimental to the nominal strength and hardness properties of the worked metal. Under the proper annealing conditions these stresses are eliminated sufficiently to give improved hardness and strength in the recovery-hardening range.

SUMMARY

1. The internal friction of single crystals of brass, copper and aluminum, and of brass specimens consisting of two and three

large grains in each specimen has been measured at low vibratory stress amplitudes after various stressing and annealing treatments.

2. A dependence of the internal friction upon crystallographic orientation was found in the single crystals of brass.

3. The increase in the internal friction associated with cold-working in single crystals of brass was found to be of a transient nature that declines with time at room temperature to the value of original unstrained specimens. In polycrystalline brass definite stable values can be associated with the amount of plastic straining in the structure.

4. The stressing of brass and aluminum crystals in tension below their respective yield points effected no increase in their internal-friction values. In fact, the values in many cases decreased as a result of this stressing to others that were lower than those obtained by annealing treatments.

5. This effect is magnified in bicrystalline and tricrystalline specimens of brass.

6. The stressing of brass single crystals in compression results in the same effects on the damping as does tensile loading.

7. There is an increase in the internal friction of copper crystals, which accompanies stressing at loads considerably below the yield point. This value declines with time. Loading above the yield point results in unmeasurably high values.

8. The results can be interpreted in term of a localized relaxation mechanism based on localized residual stresses associated with inhomogeneities, rather than on areas of inherently low shearing strength, as hypothesized by previous investigators.

9. The existence of these localized residual stresses permits an explanation of the recovery-hardening effect.

ACKNOWLEDGMENT

The author wishes to express sincere thanks to Prof. C. H. Mathewson for his interest and encouragement during this investigation.

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DISCUSSION

C. ZENER.*—Dr. Found has discussed his experimental observations upon internal friction in the light of several theories. One of these, the relaxation theory, assumes that plastic deformation introduces localized regions that cannot permanently sustain shearing stresses, and that it is the viscous flow within these regions that gives rise to internal friction. Dr. Found states that it is not apparent that this relaxation theory can explain the unstable type of internal friction, in contrast with the stable type, introduced by plastic deformation. The writer wishes to ask Dr. Found if his experiments are consistent with the viewpoint that the localized amorphous regions heal gradually at room temperature, rapidly at slightly elevated temperatures? It would be highly significant if these experiments are interpretable in terms of the amorphous slip planes introduced by Beilby and latterly discredited among metallurgists. It is to be remembered that in Rosenhain's extension of Beilby's concept these localized amorphous regions were assumed to become gradually reabsorbed into the crystalline matrix from which they were formed.

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T. A. Read.*—The author is to be congratulated for presenting a paper containing such a wealth of suggestive experimental data. The writer feels, however, that Dr. Found dismisses too hastily the interpretation of the internal friction of single crystals in terms of the formation and motion of dislocations. The author rejects the dislocation picture because the data presented in Fig. 8 fail to exhibit a direct correlation between internal friction and crystal plasticity as determined by slip-plane orientation. Such a correlation is not to be expected, however, for the quantity $1/Q$ represents essentially the ratio of the energy dissipated during a cycle of vibration to the total energy of vibration. Since at a given stress amplitude the vibration energy per unit volume is inversely proportional to the elastic modulus, it is clear that elastic anisotropy should lead to an orientation dependence of the internal friction even for a material that has the same yield strength in all crystallographic directions. Since brass is very anisotropic elastically $[E(111)/E(100) = 3.5]$, it is to be expected that this effect will exert a stronger influence on the orientation dependence of the internal friction than the varying orientation of the slip planes. On this basis, the highest internal friction is to be expected for a crystal with a (111) orientation and lowest internal friction for a (100) crystal, as found by the author. The difference between the measured ratio of the internal friction in the (111) and (100) directions and that to be expected from the elastic anisotropy may have its origin in the adjustment of the data for the frequency of measurement, which was systematically greater for crystals with orientations near (111).

G. H. Found (author's reply).—The author finds it difficult to consider these experimental observations in terms of the amorphous theory, since this theory is inconsistent with modern metallurgical thought. Dr. Zener apparently prefers to consider the relaxation theory, which requires the existence of discontinuous regions of inherent weakness in the metal structure. Some of these regions, he has suggested, may consist of amorphous material. The author prefers to consider the observations in terms of local locked-in stresses created by unique localized deformation characteristics throughout the normal metal structure. This does not require the postulation of regions within the metal whose existence it is difficult to justify. Instead, the proposed theory utilizes concepts about the metal structure which are consistent with other experimental observations.

Dr. Read has offered an explanation for the variation in the internal friction with orientation observed for the brass crystals in this investigation. He has not explained, however, the inconsistency between these observations for brass crystals and his observations on copper crystals, for which he observed no orientation dependence. Copper crystals are also elastically anisotropic $[E_{(111)}/E_{(100)} = 2.8]$.

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Recrystallization of Aluminum in Terms of the Rate of Nucleation and the Rate of Growth

By W. A. Anderson* and R. F. Mehl,† Member A.I.M.E.

(New York Meeting, February 1945)

Recrystallization of cold-worked metals has long been known to proceed by a process of nucleation and growth.[1] When a cold-worked metal is heated to a temperature at which recrystallization will ensue, nuclei of new grains, essentially strain-free, appear and grow. As the process proceeds, nuclei continue to appear and to grow, until the cold-worked matrix has been entirely consumed and recrystallization has been completed (Fig. 1). Conducted isothermally, a measurement of the fraction of the matrix recrystallized plotted against time, yields an isothermal recrystallization curve, showing the time course of the recrystallization process (Fig. 2).[2]

Evidently, then, the rate of recrystallization is determined by the rate at which nuclei form and the rate at which they grow. The rate of nucleation N is the number of nuclei that form in unit time in unit volume of the unrecrystallized matrix, and the rate of growth G is the increase in radius of the recrystallized grain per unit time. In recent years attempts have been made to determine N and G as these vary with the well-recognized variables affecting recrystallization: time, temperature, degree of deformation, etc.[1] Such studies yield information that is more fundamental than that conveyed by the conventional recrystallization diagram,[1] since the rate of recrystallization is thus analyzed into its two component rates.[3]

Methods are now available by which N and G can be measured, and analytical expressions have been developed for the interrelationships among N, G, the isothermal recrystallization curve, and the final grain size, which greatly facilitate analysis.[2–4] The application of these methods has been demonstrated recently for the recrystallization of silicon ferrite.[2]

Data on N and G in dependence upon the recognized recrystallization variables are, however, very fragmentary;* values of N and G have been determined for some metals, but the effect of temperature, which would yield the fundamentally important activation energies, has been too little studied. Thus far there has been no detailed study of the recrystallization of any one metal in terms of N and G over appreciable ranges of the variables time, temperature, degree of deformation, and original grain size. It is the purpose of the present paper to provide such a study, employing aluminum.

This paper represents part of a thesis submitted by W. A. Anderson to the Graduate Committee of the Carnegie Institute of Technology, Pittsburgh, Pa., in partial fulfillment of the requirements for the degree of Doctor of Science. Manuscript received at the office of the Institute Dec. 1, 1944. Issued as T.P. 1805 in Metals Technology, February 1945.

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† Director, Metals Research Laboratory, and Professor, Department of Metallurgical Engineering, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

[1] References are at the end of the paper.

* The literature on this subject is given in ref. 2.

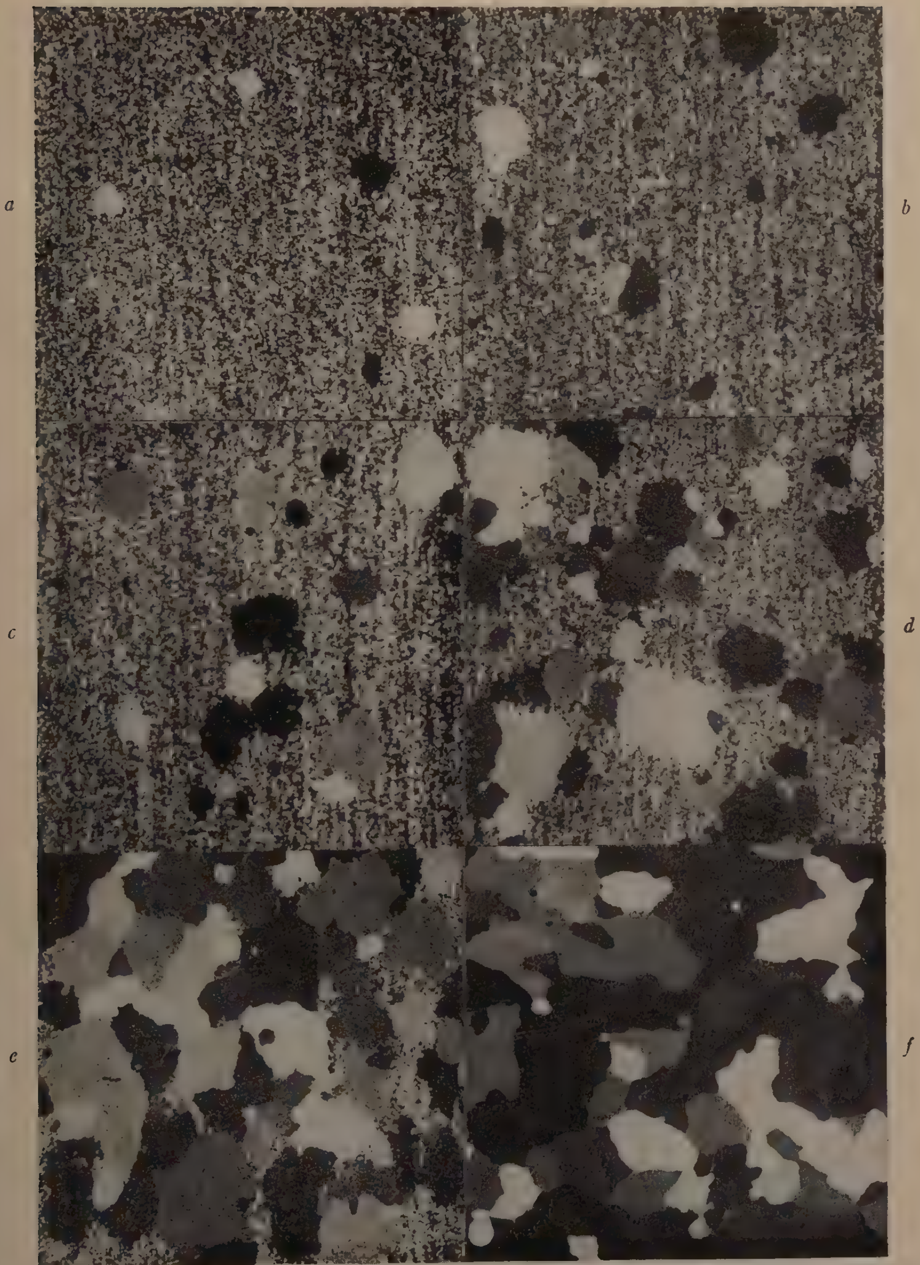

FIG. 1.—PROGRESS OF RECRYSTALLIZATION AT 310°C. IN LOT B ALUMINUM AFTER 5 PER CENT ELONGATION. × 10.

Etched with Tucker's reagent. *a,* 50 hours; *b,* 55 hours; *c,* 60 hours; *d,* 70 hours; *e,* 80 hours; *f,* 100 hours.

Materials

High-purity aluminum was used. As the work expanded it became necessary to obtain several lots of this grade of aluminum, designated as A, B, C, D, and E. The chemical compositions of these lots are given in Table 1. Lot A was used for studies on sheets 0.015 in. thick; lot B for studies on sheets 0.125 in. thick; and lots C, D and E were used in studies of the effect of the original grain size. These materials were received in the as-rolled condition; lot A had been cold-rolled 90 per cent; lot B, somewhat more than 70 per cent; lot C, 90 per cent; lot D, 50 per cent; and lot E, 25 per cent.

Table 1

Lot	Compositions and Initial Grain Sizes of the Annealed Aluminum Sheets					
	Nominal Thickness, In.	Compositions, Per Cent				Grain Size, Grains per Sq. Mm.
		Si	Fe	Cu	Ti	
A	0.015	0.008	0.0008	0.022	0.002	530
B	0.125	0.01	0.03	0.01		598
C	0.015	0.004	0.004	0.006	0.001	484
D	0.015	0.004	0.004	0.006	0.001	345
E	0.015	0.004	0.004	0.006	0.001	60

Strips 2 cm. wide and 20 to 25 cm. long were cut from this material, with the long dimension perpendicular to the direction of rolling. These cold-worked strips were recrystallized in order to provide a uniformly small and equiaxed grain size; for this purpose, lots A, B and C were annealed at 300°C. and lots D and E at 350°C. The grain sizes of the recrystallized materials are given in Table I.

Treatment

Cold deformation was supplied by simple elongation in a tensile machine. This method was chosen because of the uniformity and reproducibility with which it may be practiced, and because of the simplicity of the stress pattern produced; no macroscopic (Heyn) stresses originate—as they do, for example, in cold-rolling—but only a uniformly distributed pattern of microscopic stresses. Parallel gauge lengths 2 cm. apart were marked along the length of the strips. The distribution of elongation over the whole length of the strips was measured between these gauge marks. Each strip provided six to eight samples, each 2 by 2 cm.; the degree of elongation in the samples varying by not more than ±0.2 per cent elongation.

The elongated samples were heated for recrystallization in a fused salt bath, mechanically stirred, with automatic temperature control. Temperature variation within the bath amounted to ±1°C., while successive settings at the same temperature were accurate to ½°C. The thin sheet samples came to temperature in the bath within 2 to 3 sec., and the thick samples in about 20 sec.; both of these time periods are negligible compared with the times required for recrystallization. All measurements were made on samples recrystallized isothermally. Inasmuch as prior recovery at lower temperatures has been observed to affect the rate of recrystallization in several earlier investigations,[2] samples were introduced into the bath soon after straining in order to minimize the time available for recovery at room temperature; it was found, however, that recovery at temperatures well above room temperature had no effect upon the rate of recrystallization in this material, and this precaution was unnecessary.

"Two-dimensional" and "Three-dimensional" Recrystallization

Lot A, of a thickness of 0.015 in., was used in studying "two-dimensional" recrystallization; that is, recrystallization in which the diameter of the recrystallized grain exceeds the thickness of the sheet. Analytical methods have been developed for this case;[2] they employ a value of *N* referred to unit *area* instead of the customary unit *volume*. The thick sheets served to study "three-dimensional" recrystallization, in which the diameter of the recrystallized grain is much smaller than the thickness of the sheet, employing the usual analytical treatment,[3,4] with N referred to unit *volume*.

METHODS

Ideally, the course of recrystallization can be followed by periodic observations upon one sample at various time intervals. But this method requires repeated etching in order to display the grain structure, and it was earlier observed (and observed also in this study) that etching may impede the subsequent growth of a partially grown recrystallized grain,[2] affording erroneous results. Accordingly, the equally reliable method of statistical analysis of a series of samples, removed from the bath in groups of four to six samples at a succession of time intervals and studied separately, was employed. This method had given reliable results in the earlier study on silicon ferrite.[2] The measurements on the samples in each small group, recrystallized for the same time period, were averaged, in order to minimize errors and minor differences among the individual otherwise identical samples.

The grain structure of the 0.015-in. sheets was determined by simple observation of the surface etched with Tucker's reagent. The structure of the 0.125-in. sheet was studied after filing and polishing until the plane of polish lay halfway in the original thickness, when it was similarly etched. The structures were examined on the ground-glass screen of a metallograph at a magnification of 5 to 10. The recrystallized grains could be readily distinguished from the matrix and measurements were made upon them under two circumstances: (1) when, at low degrees of deformation, the recrystallized grain grew much larger than the matrix grains, and (2) when, at high degrees of deformation, the recrystallized grain could be distinguished by its absence of distortion from the greatly distorted matrix grains. In the first circumstance, simple elongation may be used to provide the deformation, but the range of this deformation is limited, since uniform elongation cannot be obtained at high degrees of elongation; rolling, of course, would avoid this difficulty, but would introduce the additional difficulty of complexities in the distribution of both strain and stress. There is, therefore, an intermediate range of deformation where it is difficult to make studies of this sort.

Aluminum, and also silicon ferrite, neither of which forms annealing twins, provide simple recrystallized grain structures unconfused by twins, and are favorable materials for this study. The partially recrystallized grain structures were traced on transparent paper or were photographed. Fig. 1 shows a series of samples illustrating the progress of recrystallization as a function of time. From these tracings or photographs the areas of the recrystallized grains were determined either planimetrically or by superimposing the outlines of the grains on coordinate paper and counting squares. The areas of many small grains, however, were determined simply by matching with tracings of grains of predetermined areas.

From the data accumulated in this manner, it is possible, as shown below, to determine (1) the fraction recrystallized as a function of time, yielding isothermal recrystallization curves, (2) the rate of nucleation N, and (3) the rate of growth G. These are the data required.

RECRYSTALLIZATION OF THIN SHEET—"TWO-DIMENSIONAL" RECRYSTALLIZATION

Strips of lot A, 0.015 in. thick, were elongated in tension 1.9 per cent, 2.8 per cent, 5.1 per cent, 7.8 per cent, and 10.6 per cent, and recrystallized isothermally at a series of temperatures between 283° and

400°C. This provided recrystallized grains, which grew many times larger than the matrix grains, of a diameter that indeed exceeded the sheet thickness; this is "two-dimensional" recrystallization. Cross sections of partially recrystallized samples showed that the new grains had originated in nuclei located both at the surface and within the volume of the sample, but with some preference for the sheet surface; there was not, however, a marked preference for surface nucleation, as observed in silicon ferrite.[2] Grains that had nucleated on one surface exhibited a larger grain area on that surface than on the opposite surface; in such cases these two areas were averaged.

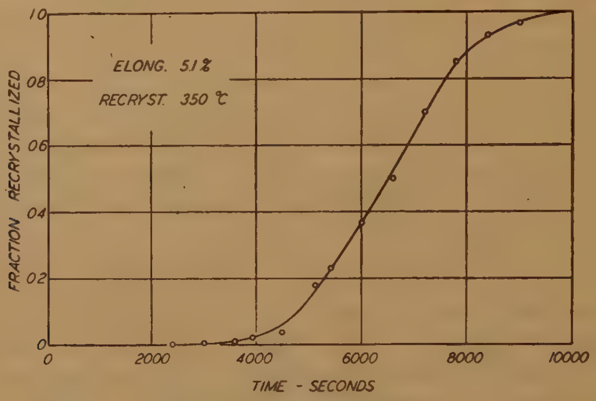

Fig. 2.—Isothermal recrystallization curve.
Fraction recrystallized versus time at 350°C., 5.1 per cent elongation. Lot A aluminum.

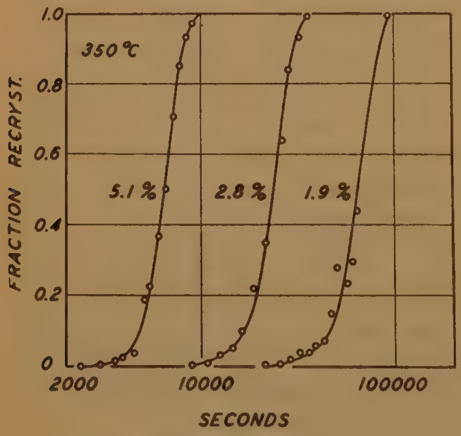

Fig. 3.—Isothermal Recrystallization curves at 350°C.
Showing effects of increasing degrees of deformation. Lot A aluminum.

Fig. 2 illustrates the type of isothermal recrystallization curve obtained, with the fraction recrystallized plotted against time. This is similar in shape to curves obtained for silicon ferrite; it is the type of curve expected for general nucleation[3] and is observed familiarly in the formation of pearlite from austenite at high temperatures.[4,5] All curves obtained for the recrystallization of aluminum at low degrees

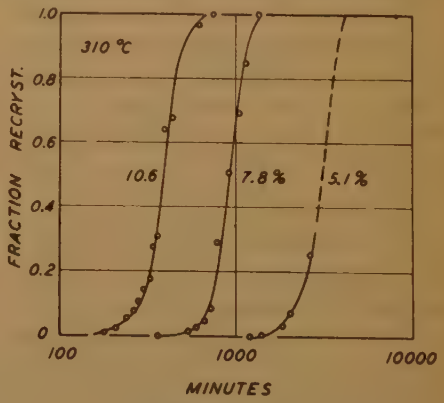

Fig. 4.—Isothermal recrystallization curves at 310°C.
Showing effects of increasing degrees of deformation. Lot A aluminum.

of deformation have a similar shape; an example of a different shape will be shown for recrystallization following a high degree of deformation.

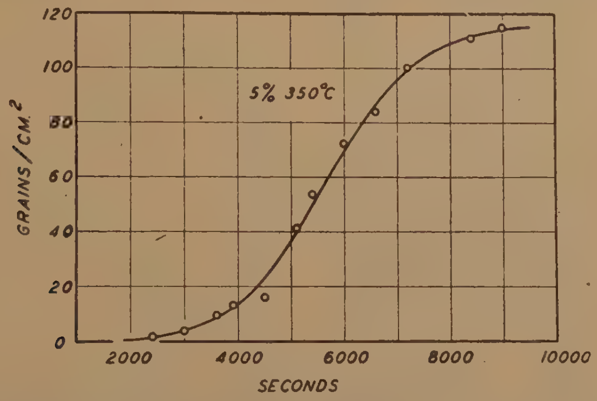

FIG 5.—NUMBER OF RECRYSTALLIZED GRAINS VERSUS TIME AT 350°C., 5.1 PER CENT ELONGATION. LOT A ALUMINUM.

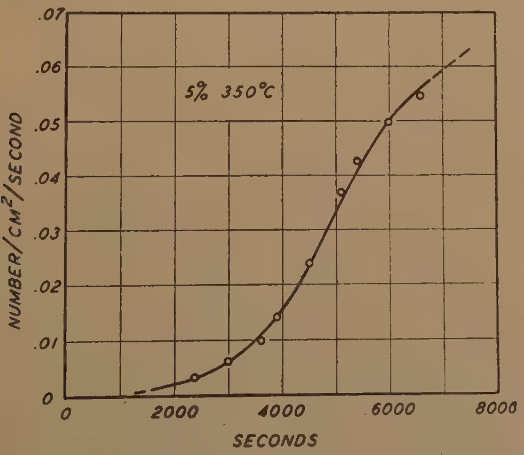

FIG. 6.—RATE OF NUCLEATION VERSUS TIME AT 350°C., 5.1 PER CENT ELONGATION. LOT A ALUMINUM.

The effect of the degree of deformation on the isothermal rate of recrystallization at constant temperature is shown in Figs. 3 and 4. It is evident that the rate of recrystallization is the greater, the greater the degree of deformation and the higher the temperature. This is in accordance with older information.

The rate of nucleation can be calculated from the data. The number of new grains appearing as a function of time can readily be plotted, as in Fig. 5. For "two-dimensional" recrystallization the rate of nucleation N at any time period is simply the slope of this curve at that time period, divided by the fractional area of the unrecrystallized matrix at the same time period (since N is the number of grains formed per unit time—one second—in unit area—one sq. cm.—of unrecrystallized matrix). Fig. 6 is the curve of N versus time obtained from Fig. 5. Fig. 5 shows that the number of grains increases with time of recrystallization, and Fig. 6 shows that the derived curve of N behaves similarly, to approximately 65 per cent of complete recrystallization. Data beyond this point are not included, since the errors appear to become too serious. Five additional pairs of curves of this sort were obtained for different degrees of deformation and different recrystallization temperatures, though extending only to 30 to 40 per cent of complete recrystallization. In all cases N was found to increase approximately exponentially with time (as in silicon ferrite[2]), and this rate of increase was the greater, the greater the degree of deformation and the higher the temperature.

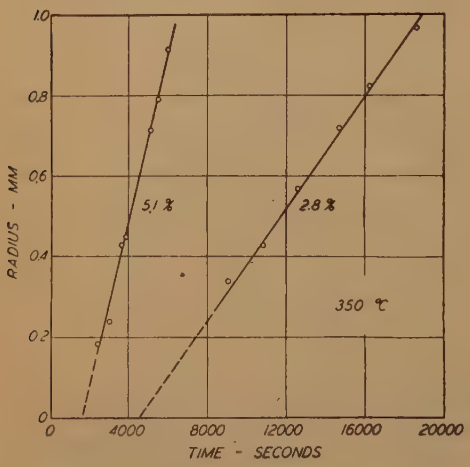

FIG. 7.—RADIUS OF LARGEST GRAIN VERSUS TIME OF HEATING AT 350°C., 2.8 AND 5.1 PER CENT ELONGATION. LOT A ALUMINUM.

The rate of growth G was determined by plotting the radius of the largest grain (which had not impinged on another growing grain) observed in a series of samples recrystallized for different time periods. Under the assumption that the largest grains nucleated first, all of the largest grains nucleated at this same time instant, and a plot of their radii versus time should give G. Fig. 7 is such a plot; the slope of this curve expressed in centimeters per second is G. It is observed here, and also in all other cases, that this curve is a straight line; that is, that G is independent of time. This curve intersects the time axis, determining an initial time period that has been called the "induction period," or "incubation period." This phenomenon, studied in some detail by Kornfeld (see bibliography in ref. 2), will be discussed later. Fig. 7 also shows that the induction period is the smaller, the greater the degree of deformation; and that G is the greater, the greater the degree of deformation.

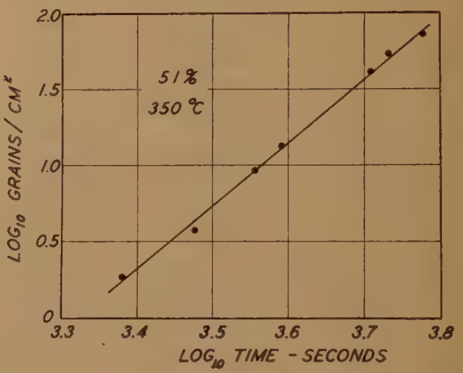

FIG. 8.—NUMBER OF RECRYSTALLIZED GRAINS VERSUS TIME AT 350°C. LOGARITHMIC SCALE. 5.1 PER CENT ELONGATION. LOT A ALUMINUM.

These methods of determining N and G are exceedingly laborious. In order fully to survey the effects of the important variables upon N and G, abbreviated methods of analysis were adopted. Obviously, since G is constant with time, as shown, only two points on curves of the type of Fig. 7 are necessary to determine G, and this procedure was adopted. For N, an abbreviation can be obtained in the following manner: In all cases N varies approximately exponentially with time, at least up to about 30 per cent recrystallization, and this may be written

$$\ln N = \ln a + bt \qquad [1]$$

in which a and b are constants.[2] In all cases the number of grains n increases with time in the same time period, by a function of the type

$$\ln n = \ln c + d \ln t \qquad [2]$$

in which c and d are constants. The validity of this function is shown in Fig. 8. The determination of n at two time periods, preferably at 1 to 5 per cent and 20 to 25 per cent recrystallization, will serve to establish the whole curve, and thus to calculate n at any time period. From these values of n, N can be calculated for any time period for which the fraction recrystallized is known; two such points will establish the constants of Eq. 1 and thus will also establish the full curve of N versus time. This is the procedure adopted. The calculated values of the terms in these equations are listed in Table 2. It will be shown later that these values of N for the thin sheet can be calculated to N for thick sheets; i.e., can be expressed on a volume basis in the usual way.

EFFECT OF TEMPERATURE AND EFFECT OF DEFORMATION

In establishing the effect of any variable upon N, it must be remembered that N varies with time and therefore does not invite a direct and simple comparison. In order to select single but comparable values of N for studying the effect of a variable upon it—e.g., the effect of temperature—N values were selected from the curves for N versus time, at points on the several curves where the samples had recrystallized 20 per cent. Other

TABLE 2.—*Rate of Nucleation and Rate of Growth for "Two-dimensional" Recrystallization*

Temperature, Deg. C.	$\ln N = \ln a + bt$		$R = G(t - I.P.)$[a]		N, No. per Sec. per Sq. Cm.	
	a	b	G, Cm. per Sec.	Induction Period, Sec.	At 10 Per Cent Recryst.	At 20 Per Cent Recryst.
			1.9 Per Cent Elongation			
350	1.85×10^{-4}	4.4×10^{-5}	2.15×10^{-6}	7,500	1.5×10^{-3}	2.1×10^{-3}
370	7.4×10^{-4}	2.15×10^{-4}	9.35×10^{-6}	1,400	6.8×10^{-3}	9.5×10^{-3}
400	1.85×10^{-2}	2.5×10^{-3}	8.15×10^{-5}	225	0.15	0.22
			2.8 Per Cent Elongation			
308	3.1×10^{-6}	3.9×10^{-6}	1.9×10^{-7}		6.2×10^{-5}	9.0×10^{-5}
328	3.85×10^{-5}	2.05×10^{-5}	1.05×10^{-6}	25,500	4.6×10^{-4}	6.5×10^{-4}
350	4.5×10^{-4}	1.45×10^{-4}	7.0×10^{-6}	4,500	4.7×10^{-3}	6.5×10^{-3}
370	1.1×10^{-3}	1.15×10^{-3}	3.35×10^{-5}	1,000	3.7×10^{-2}	5.2×10^{-2}
400	1.9×10^{-2}	5.9×10^{-3}	1.5×10^{-4}	120	0.34	0.48
			5.1 Per Cent Elongation			
310	6.75×10^{-6}	3.7×10^{-5}	9.15×10^{-7}	42,000	8.2×10^{-4}	12.5×10^{-4}
328	5.3×10^{-5}	1.4×10^{-4}	3.3×10^{-6}	11,600	6.2×10^{-3}	8.8×10^{-3}
350	1.4×10^{-3}	6.35×10^{-4}	2.15×10^{-5}	1,600	2.6×10^{-2}	3.8×10^{-2}
370	3.35×10^{-3}	3.55×10^{-3}	9.75×10^{-5}	450	0.17	0.24
			7.8 Per Cent Elongation			
283	3.15×10^{-6}	1.25×10^{-5}	1.95×10^{-7}	130,000	4.7×10^{-4}	6.7×10^{-4}
310	2.1×10^{-5}	1.3×10^{-4}	1.6×10^{-6}	13,800	5.9×10^{-3}	1.1×10^{-2}
350	1.4×10^{-3}	2.05×10^{-3}	4.3×10^{-5}	800	0.10	0.15
370	4.4×10^{-3}	8.2×10^{-3}	2.0×10^{-4}	260	0.50	0.71
			10.6 Per Cent Elongation			
283	3.45×10^{-5}	1.8×10^{-5}	2.85×10^{-7}	43,000	1.7×10^{-3}	2.0×10^{-3}
310	4.8×10^{-4}	1.7×10^{-4}	3.5×10^{-6}	3,000	1.6×10^{-2}	2.3×10^{-2}
328	2.6×10^{-4}	9.4×10^{-4}	1.35×10^{-5}	2,000	5.6×10^{-2}	7.9×10^{-2}

[a] R = radius of recrystallized grain at time t; $I.P.$ = induction period.

comparable points could have been taken—for example, 10 per cent—but it was found that such plots yield equivalent results for the temperature coefficient of N. Table 2 gives values of N for different temperatures at time periods for 10 and 20 per cent recrystallization. These data show N to increase rapidly with increasing temperature.

Since G is invariant with time* it is easy to compare values of G. Table 2 gives data showing the temperature variation of G. It is observed that G also increases rapidly with temperature.

The temperature dependence of N and that of G are shown in Figs. 9 and 10, where the logarithm of N (or G) is plotted as a function of the reciprocal of the absolute temperature. These functions may be written

$$\ln N = \ln A - \frac{Q_N}{RT}, \qquad \text{or}$$

$$N = A \times e^{-\frac{Q_N}{RT}} \qquad [3]$$

$$\ln G = \ln B - \frac{Q_G}{RT}, \qquad \text{or}$$

$$G = B \times e^{-\frac{Q_G}{RT}} \qquad [4]$$

where T is the absolute temperature, R the gas constant, A and B are constants, and Q_N and Q_G are constants expressed in calories when R is expressed in calories per degree; $\frac{Q_N}{R}$ and $\frac{Q_G}{R}$ are the temperature coefficients. Within the limits of experimental error, Q_N, which is derived from the slope of the curves in Fig. 9, is independent of the degree of recrystallization chosen as a basis of comparison for values of N. The constant A, in Eq. 3, however, varies with the percentage of recrystallization chosen; i.e., A varies directly as does the value of N with the degree of recrystallization. Choosing N at lower percentage of recrystallization merely displaces the curves in Fig. 9 downward without altering their slope. The constant B in Eq. 4 is not subject to such variations, since G does not vary with time and percentage of recrystallization.

Exponential relationships of the type given by Eqs. 3 and 4 are familiar in the study of reaction rates, and already have been employed in dealing with data on N and G (see bibliography in ref. 2) in theories of recrystallization (see, for example, refs. 6 and 7) and in the allied field of diffusion.[8] The Q values are designated as "activation energies," representing in the case of Q_N the energy originating in thermal fluctuations required to enable atoms to move from their positions in the distorted lattice and to form a nucleus of the recrystallized grain, and in the case of Q_G representing the energy necessary to enable atoms to move from their positions in the distorted lattice at the growing interface of the recrystallized grain and to attach themselves to and become an integral part of the growing recrystallized grain.*

The values of Q_N and Q_G for various degrees of deformation are listed in Table 3.

TABLE 3.—*Values of Constants A, B, Q_N and Q_G for "Two-Dimensional" Recrystallization*

Percentage of Elongation	A (20 Per Cent Recryst.), No. per Sec. per Sq. Cm.	Q_N, Calories	B, Cm. per Sec.	Q_G, Calories
1.9	9.4×10^{24}	79,000	7.5×10^{15}	61,500
2.8	1.3×10^{23}	72,000	2.6×10^{16}	61,500
5.1	1.3×10^{20}	61,000	1.5×10^{16}	59,000
7.8	8.5×10^{18}	56,000	5.4×10^{15}	57,500
10.6	8.0×10^{17}	52,000	4.3×10^{15}	56,500
20.0			1.0×10^{14}	51,500

The effects of the degree of deformation on N and G are reported in Table 2. They

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* All recent careful studies of G confirm its independence of time; see bibliography in ref. 2.

* Something more will be said later concerning these matters. Nucleation theory for truly heterogeneous reactions was reviewed in ref. 9; nucleation theory for recrystallization is a less satisfactory state, as shown later.

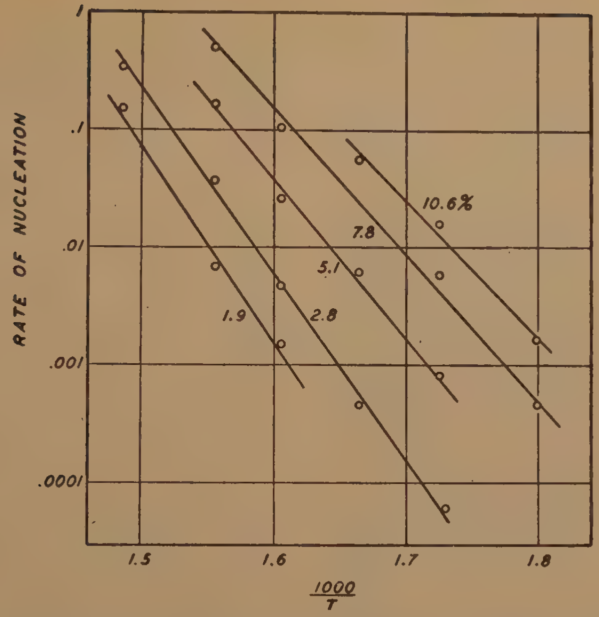

FIG. 9.—LOGARITHM OF RATE OF NUCLEATION AT 20 PER CENT RECRYSTALLIZATION VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE. LOT A ALUMINUM.

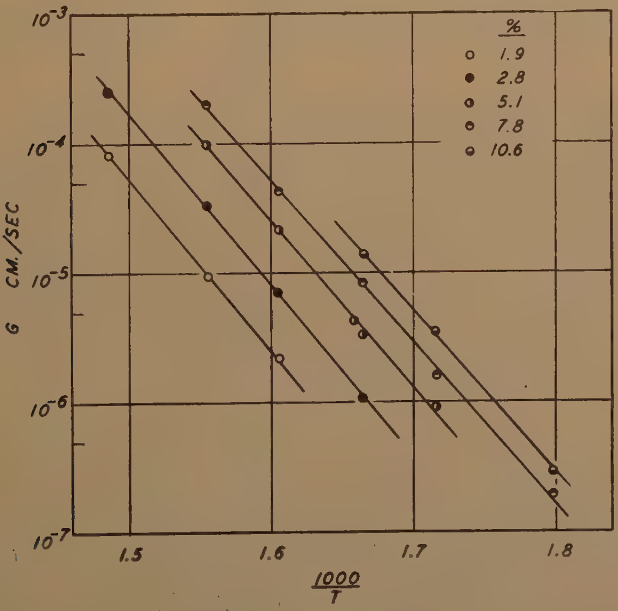

FIG. 10.—LOGARITHM OF RATE OF GROWTH VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE. LOT A ALUMINUM.

are given graphically in Figs. 11, 12 and 13. These data are limited to a range from zero to 10.6 per cent elongation, for the reasons given earlier. Both N and G increase with increasing deformation. The effect of degree of deformation on G is interesting: G increases with increasing deformation up to about 10 per cent (plotted here as effective strain, which differs little in this range from simple elongation); beyond 10 per cent, G still increases but at a decelerating rate. This suggests that a maximum is approached at a high degree of strain, a possibility for which some support will be given later.

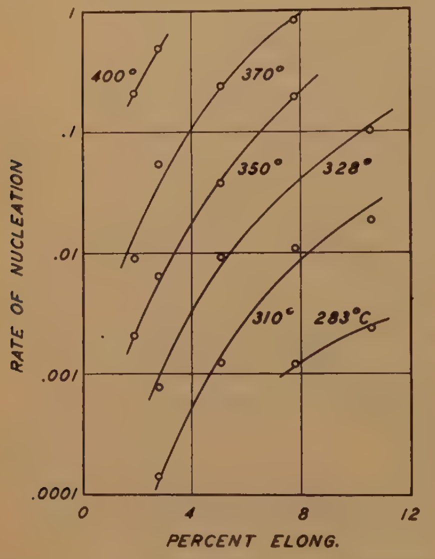

Fig. 11.—Logarithm of rate of nucleation at 20 per cent recrystallization versus the percentage of elongation. Lot A aluminum.

The induction period is plotted in Fig. 13 as a function of degree of deformation. The so-called induction period, estimated as shown earlier, has been variously interpreted (see Kornfeld references in ref. 2) and often an importance is ascribed to it which seems to be beyond its merits, as discussed later.

The temperature coefficients of N and G, as shown by Q_N and Q_G, are also dependent upon the degree of deformation. This is shown by the data in Table 3, in which

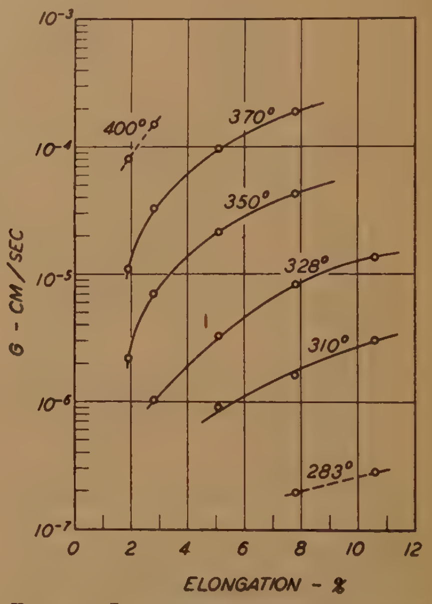

Fig. 12.—Logarithm of rate of growth versus percentage of elongation. Lot A aluminum.

the constants in Eqs. 3 and 4 are reported, and in Fig. 14, where the activation energies Q_N and Q_G are plotted as functions of the degree of deformation. These data show that the rate constants A and B and the activation energies Q_N and Q_G decrease with increasing amounts of deformation.

Isothermal Rate of Recrystallization

The isothermal recrystallization curve, as shown in Figs. 2 and 15, is determined by the cooperation of N and G. The functional relationships among N, G, the isothermal reaction curve, and the final grain size have already been developed for nucleation and growth processes generally[3] and have been further developed to apply to "two-dimensional" recrystallization.[2] It has been shown that the isothermal curve for the latter case can be satisfactorily calculated from determined values of N and G for recrystallization in silicon ferrite.[2]

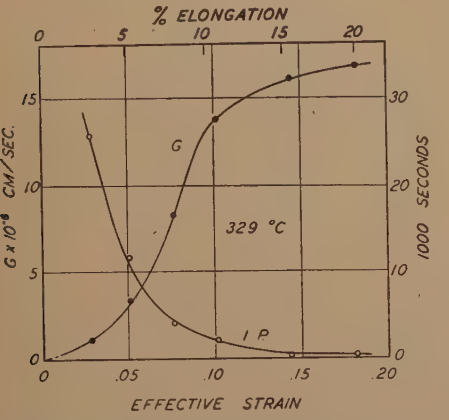

FIG. 13.—RATE OF GROWTH AND INDUCTION PERIOD AT 329°C. AS FUNCTIONS OF DEGREE OF STRAIN. LOT A ALUMINUM.

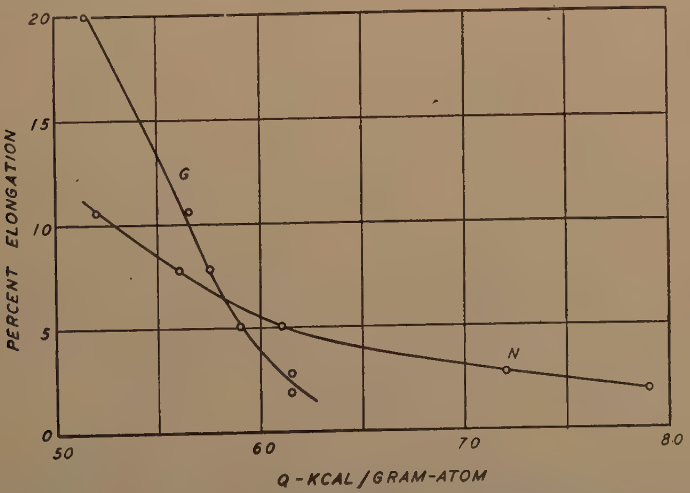

FIG. 14.—ACTIVATION ENERGIES FOR TWO-DIMENSIONAL NUCLEATION AND GROWTH VERSUS PERCENTAGE OF ELONGATION. LOT A ALUMINUM.

For the present case the analytical expressions assume that: (1) recrystallization is "two-dimensional," (2) N increases exponentially with time, (3) G is constant with time, and (4) nuclei grow to perfect circles.

It has been shown that these assumptions are reasonably correct in the present case. However, N increases exponentially with time accurately only up to about 30 per cent recrystallization. The nuclei formed during this time period play a predominant role in determining the time course of recrystallization (as compared with those that form later; and, having less time to grow, account for only a small fraction of the finally recrystallized sample) and accordingly assumption 2 is adequate as a good approximation. Moreover, as may be seen in Fig. 1, the growing recrystallized grains are not always circular in shape; frequently they are elliptical in a direction parallel to the original rolling direction of the sheet. The ellipticity observed during the growth of a recrystallized grain, however, is not manifest in the structure of the finally recrystallized sample, for this is observed to be equiaxed. The ratio of major to minor axes in the elliptical growing grains was rarely greater than 1.5 and usually less. Errors in the calculation of the recrystallization curve from this source are small compared with those arising from departures from the assumed exponential relationship between N and time, and arising from departures in reality from the ideal of two-dimensional recrystallization.

On these assumptions, the time course of isothermal recrystallization for two-dimensional recrystallization is given by:

$$f(t) = 1 - e^{-\frac{2\pi G^2 a}{b^3}\left(e^{bt} - \frac{b^2t^2}{2} - bt - 1\right)} \qquad (5)$$

where $f(t)$ is the fraction recrystallized at times t; G is the rate of growth, and a and b are the constants of the exponential nucleation equation 1. Thus by introducing determined values of G, a, and b it should be possible to calculate the experimental recrystallization curves of Figs. 2, 3 and 4. The result of one such calculation is given in Fig. 15 with the values of G, a and b taken from Table 2. The agreement between the calculated and determined curves is fair.

The agreement is least good at low degrees of recrystallization. In other comparisons, however, the calculated points were found to lie both to the right and to the left of the observed curve, at different degrees of recrystallization, and little can be said concerning the reasons for the difference, which in any event is relatively minor.

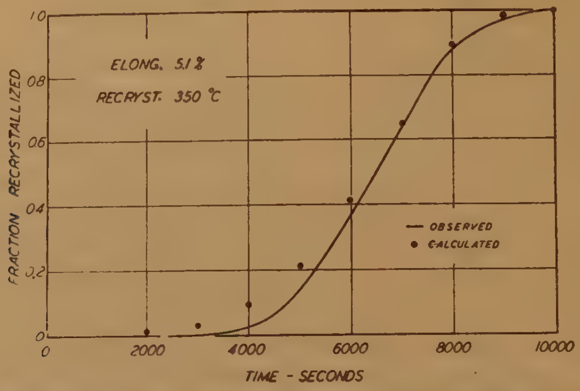

FIG. 15.—COMPARISON OF CALCULATED AND EXPERIMENTAL RECRYSTALLIZATION CURVES. LOT A ALUMINUM.

RECRYSTALLIZATION OF THICK SHEET—"THREE-DIMENSIONAL" RECRYSTALLIZATION

While "two-dimensional" recrystallization is observed in practice, as in silicon ferrite, engineering practice usually attempts to produce "three-dimensional" recrystallization, in order that the deleterious effects of a grain size that is large compared with the section thickness may be avoided.[10] The present study was extended to include a study of N and G in the three-dimensional recrystallization of aluminum.

Lot B (Table 1) was employed, of a thickness of 0.125 in. The grain size of the starting material is given in Table 1, and is substantially the same as that employed in the two-dimensional studies. Strips of this material were similarly elongated, 5 per cent, 10 per cent, and 15 per cent in tension, and recrystallized at 310°, 325°, 350° and 370°C. The degree of recrystallization, taken from a plane midway in the sheet thickness, was estimated by tracings, as before. The recrystallized grain as seen on this plane conformed closely to a circle, up to the time of impingement with neighboring growing grains; on a perpendicular plane, however, a slight ellipticity appeared (never greater than 1.5), the degree of which was greatest in the samples elongated 5 per cent and least with those elongated 15 per cent. Again, as in the 0.015-in. sheet, this initial ellipticity tended to disappear as complete recrystallization was approached. Interestingly, nucleation appeared to show a slight preference for the center of the sheet, rather than the surface as in two-dimensional recrystallization.

The determination of N is more difficult in this case. Methods, however, have already been explored.[4] Briefly, the method adopted here consisted of the following (compare ref. 4): A plane distribution curve of the numbers and the sizes of recrystallized grains on the surface of polish was constructed, using only partially recrystallized samples in which impingement was negligible. From this plane distribution curve, a spatial distribution curve was calculated[11] and the number of grains per unit volume was obtained. A series of such curves for different times of isothermal recrystallization provided the number of grains as a function of time, from which N as a function of time could be calculated, as before.

Again, this is an exceedingly laborious method—in fact, even more time-consuming than in the earlier case—and again a shorter method was adopted for most of the work. This method assumes a constant G; knowing G, each size group of grains on the spatial distribution curve

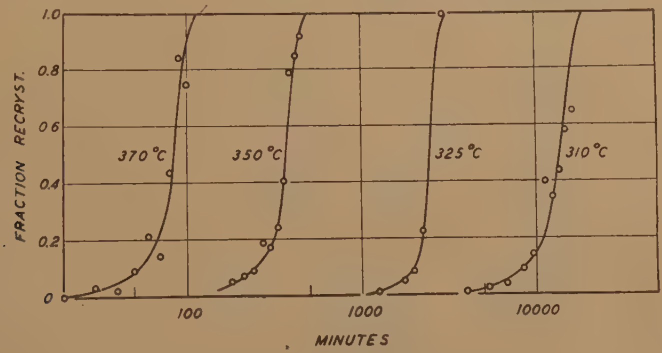

FIG. 16.—ISOTHERMAL RECRYSTALLIZATION CURVES FOR SAMPLES 0.125 INCH THICK ELONGATED 5 PER CENT. LOT B ALUMINUM.

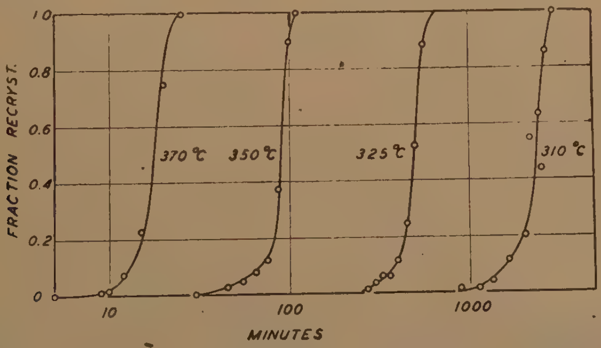

FIG. 17.—ISOTHERMAL RECRYSTALLIZATION CURVES FOR SAMPLES 0.125 INCH THICK ELONGATED 10 PER CENT. LOT B ALUMINUM.

can be related to a definite time of nucleation. The value of N is then determined from the number of grains in each size group and from the degree of recrystallization at the time at which they are nucleated.

TABLE 4.—*Rate of Nucleation and Rate of Growth for "Three-dimensional" Recrystallization*

Temperature, Deg. C.	$\ln N = \ln a + bt$		$R = G(t - I.P.)^a$		N, No. per Sec. per Cu. Cm.	
	a	b	G = Cm. per Sec.	I.P., Sec.	At 5 Per Cent Recryst.	At 10 Per Cent Recryst.
5 Per Cent Elongation						
310	3.8×10^{-5}	8.6×10^{-6}	2.1×10^{-7}	105,000	1.8×10^{-3}	2.5×10^{-3}
325	6.3×10^{-4}	2.75×10^{-5}	1.0×10^{-6}	33,000	1.15×10^{-2}	2.0×10^{-2}
350	2.0×10^{-3}	2.8×10^{-4}	5.7×10^{-6}	2,500	5.0×10^{-2}	0.135
370	1.4×10^{-2}	1.8×10^{-3}	2.15×10^{-5}	100	1.0	1.3
10 Per Cent Elongation						
310	2.3×10^{-3}	3.45×10^{-5}	8.0×10^{-7}	25,000	0.05	0.09
325	8.5×10^{-3}	1.5×10^{-4}	4.2×10^{-6}	7,800	0.17	0.28
350	3.3×10^{-2}	9.0×10^{-4}	2.0×10^{-5}	1,000	0.85	1.55
370	1.2	2.9×10^{-3}	8.6×10^{-5}	270	8.5	10.80
15 Per Cent Elongation						
325	7.4×10^{-2}	3.8×10^{-4}	4.6×10^{-6}	1,500	1.7	
350	2.75	1.25×10^{-3}	2.7×10^{-5}	0	11.0	14.5
370	5.1	6.45×10^{-3}	1.1×10^{-4}	60	40.0	61.0

[a] R = radius of recrystallized grain at time t; $I.P.$ = induction period.

The value of G, as before, was obtained from measurements of the largest grains on a series of samples exhibiting increasing degrees of partial recrystallization. In "three-dimensional" recrystallization, this method can be used successfully providing a sufficiently large area of sample (or samples) is examined so that the largest grain in each case may be observed at its maximum diameter on the plane of polish.

EFFECT OF TEMPERATURE AND EFFECT OF DEFORMATION

The isothermal recrystallization curves obtained are given in Figs. 16, 17, and 18 for a number of temperatures, and for 5 per cent, 10 per cent and 15 per cent elongation, respectively. As was to be expected, the rate of recrystallization is the greater the higher the temperature and the greater the degree of deformation; this originates in the observed increase in both N and G with increasing temperature and with increasing degree of deformation. These results are tabulated in Table 4 and shown graphically in Figs. 19, 20, and 21.

In "three-dimensional" recrystallization, nuclei form throughout the volume, and N is expressed as the number of nuclei formed per second per unit *volume* of the unrecrystallized matrix. Values of N increase with time of recrystallization in an exponential manner, as observed in the case of "two-dimensional" recrystallization.

The constants of the exponential function for N, Eq. 1, are given in Table 4, and values for N at 5 and 10 per cent recrystallization are also listed. Values of N at higher degrees of recrystallization could not be determined, owing to the usual difficulty of the impingement of growing grains and the difficulty this causes in deriving spatial distribution curves from plane distribution curves; the difficulty here is even greater than in the study of pearlite,[4] for in the present case recrystallized grains are recognized only after they become bigger than the matrix grains, and accordingly the distribution curves are not complete in the low ranges of sizes.

The values of *N* at 5 and 10 per cent recrystallization vary exponentially with temperature, as with "two-dimensional" recrystallization; and the values of *N* increase with increasing deformation, as shown in Fig. 21. Values of *G* also increase exponentially with temperature, and increase with degree of deformation, in the manner shown in Fig. 21.

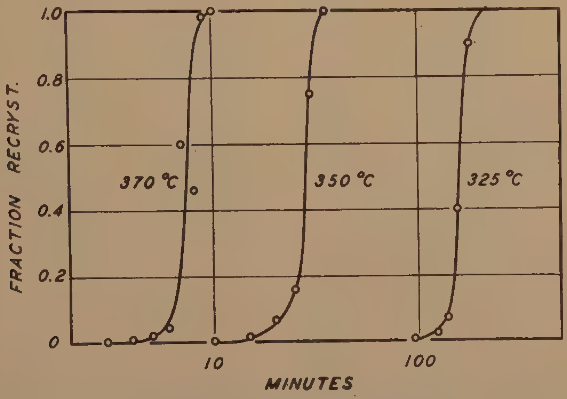

FIG. 18.—ISOTHERMAL RECRYSTALLIZATION CURVES FOR SAMPLES 0.125 INCH THICK ELONGATED 15 PER CENT. LOT B ALUMINUM.

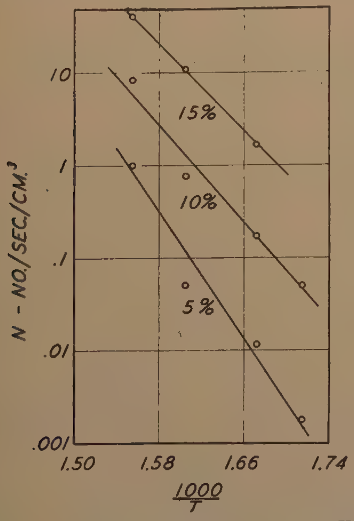

FIG. 19.—LOGARITHM OF RATE OF NUCLEATION AT 5 PER CENT RECRYSTALLIZATION VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE. LOT B ALUMINUM.

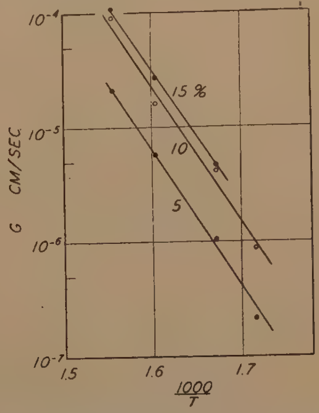

FIG. 20.—LOGARITHM OF RATE OF GROWTH VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE. LOT B ALUMINUM.

A comparison of these results on thick sheet of lot B with those obtained earlier on thin sheet of lot A shows some differences, as follows: (1) the thick sheet required appreciably longer times for equal degrees of recrystallization, (2) the values of *G* are smaller for the thick sheet than for the thin sheet, and (3) the activation energies (*Q*-values) for *N* are greater for the thick than for the thin sheet, though the activation energies for *G* are the same;

N-values are not directly comparable, as noted below.

In view of the possibility that these differences might originate in differences in history and in the slight differences in composition between lots A and B noted in Table 1, the 0.125-in. material of lot B was rolled to 0.015 in., treated to give the same initial grain size, and its recrystallization behavior studied in comparison with that of thick sheets of the same lot. Comparative isothermal recrystallization curves are given for the thin sheet from lots A and B, respectively, in Fig. 22, for 5 per cent elongation and for recrystallization at 350°C. The agreement between the two curves is fair but does indicate a small but perhaps real difference, with lot A recrystallizing a little more rapidly than lot B. Both *N* and *G* are slightly higher in thin sheets of lot A than in thin sheets of lot B, accounting for the shorter recrystallization time of lot A.

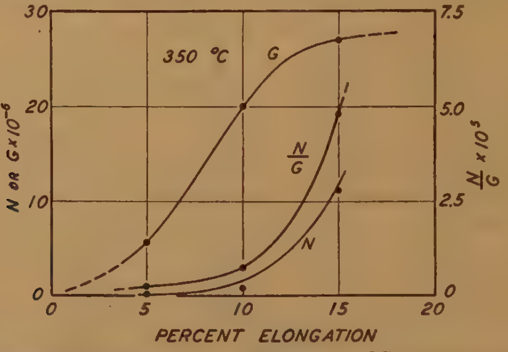

FIG. 21.—RATE OF NUCLEATION AND RATE OF GROWTH AT 350°C. VERSUS PERCENTAGE OF ELONGATION. LOT B ALUMINUM.

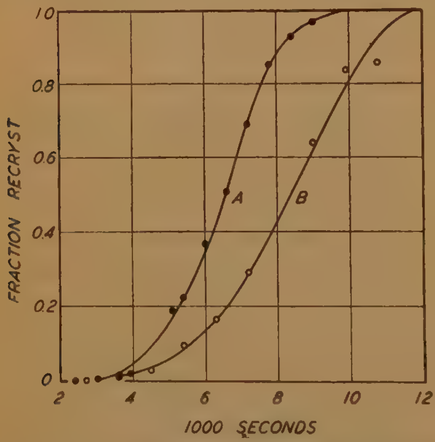

FIG. 22.—ISOTHERMAL RECRYSTALLIZATION CURVES FOR LOTS A AND B ALUMINUM AT 350°C., 5 PER CENT ELONGATION, 0.015-INCH SHEET.

It is important to note, however, that the times for the completion of recrystallization in the sheet 0.015 in. thick of both lots A and B are about one third of that needed for recrystallization of lot B in sheet 0.125 in. thick (Fig. 16). The value of *G* in the thick sheet of lot B is 5.7×10^{-6} cm. per sec. and in the thin sheet of lot B is 15.6×10^{-6} cm. per sec; values of *N* (when the *N* values of thin and thick sheet are placed on a comparable basis as shown below) at short times is somewhat higher in lot B, though at longer times the values become identical,—these differences in *N* and *G* account for the faster recrystallization of the thin sheet. There is thus a distinct difference in the behavior of lot B in the two thicknesses.

Direct comparisons of the rates of nucleation in the "two-dimensional" recrystallization (thin sheet) and "three-dimensional" recrystallization (thick sheet) are not readily made. The *N*-values are expressed in different ways in the two cases; moreover, there is a fundamental difference in the nature of nucleation in the two cases. The value of N in the thin sheets of lot B at 10 per cent recrystallization on recrystallizing at 350°C. after 5 per cent elongation is 0.02 per sq. cm. per sec.; in the thick sheet of the same material, under the same conditions, N is 0.135 per cu. cm. per sec. Consider the meaning of N in the thin material: it refers to the number of nuclei formed per unit area. Since observation shows that the growing grain attains a diameter much greater than the sheet thickness, all nuclei forming in this thin sheet are counted on the surface; correcting this number to a thickness of 1 cm. would give a value for N on the basis of *unit volume;* this value is 0.50 per cu. cm. per sec., a value larger than that exhibited by the thick sheet (see above).

But the nuclei that appear on the surface of these sheets can come only from below that surface, whereas when grains are counted in the mid-section of a recrystallized piece the grains come from both above and below that section. Accordingly, thin sheet, with an *inherent* rate of nucleation equal to that of a thick sheet would show a smaller rate of nucleation, by one half. Thus, when N is determined by counting grains on the *surface* of a recrystallized piece the observed value of N should be multiplied by 2 to obtain a value truly comparable to that determined at some mid-section. Furthermore, if the grains grow fairly large, grains nucleated at a depth greater than 0.015 in. in the present case (had there been material there) would have contributed somewhat to the observed number of grains. Therefore, the rate of nucleation observed in these thin sheets should be somewhat less than one half that in thick material studied in mid-section. For these reasons, thin sheet should recrystallize more slowly than thick sheet, under otherwise wholly identical circumstances.

In the present case, however, this further correction of N, from 0.5 c.c. per sec. to 1.0/c.c. per sec. (or slightly above) provides a value markedly greater than that actually observed in the thick sheet, namely, 0.135 c.c. per sec. This comparison, however, serves only for N values compared at 10 per cent recrystallization. At higher percentages of recrystallization the value of N for the thin sheet agrees closely with that observed for the thick sheet. This matter requires separate and detailed investigation.

The fact that G is greater in the thin than in the thick sheet of lot B requires some special explanation. This may lie in a distinct difference, observed by X-ray diffraction, in the degrees of preferred orientation in the beginning materials: the degree of preferred orientation is greater in the thin sheet than in the thick. It appears, then, that high values of G accompany high degrees of preferred orientation, and this relationship may be causal, inasmuch as (1) the values of N and G in single crystals of aluminum are dependent upon the orientation of the crystal with respect to the direction of straining,[12] and (2) G is dependent upon the crystallographic direction.[13] Thus this would seem to add an additional variable—the degree of preferred orientation in the beginning material—in recrystallization behavior.

ISOTHERMAL RECRYSTALLIZATION CURVE

In the case of "three-dimensional" recrystallization the calculated curves are based on the relationship[3]:

$$f(t) = 1 - e^{-\frac{8\pi G^3 a}{b^4}\left(e^{bt} - \frac{b^3t^3}{6} - \frac{b^2t^2}{2} - bt - 1\right)} \qquad [6]$$

in which the terms have the same significance as those in Eq. 5, and is based on the same assumptions, except that N is in terms of volume and the grains are assumed to grow to spheres. The measured values of the constants are given in Table 4.

The agreement between the calculated and observed curves is not as good as that for two-dimensional recrystallization. This would appear to originate in the greater errors in the determination of N (which is more difficult in the three-dimensional case) and in the fact that N is determined for relatively shorter time periods, making the values of the exponential constants more subject to error. The majority of the calculated curves lie to the left of the observed curves, suggesting that the experimentally determined rates of nucleation are somewhat high.

RATE OF RECRYSTALLIZATION

It may be shown from the data in Figs. 16, 17 and 18 that the time for 50 per cent recrystallization can be related to the temperature of recrystallization by the equation

$$\ln \frac{1}{t_{0.50}} = \ln C - \frac{Q_R}{RT} \qquad [7]$$

where $t_{0.50}$ is the time for 50 per cent recrystallization, C is a constant, Q_R is a quantity similar to an activation energy now applying to the over-all recrystallization process, and the remaining terms have the same significance as in Eqs. 3 and 4.* This equation can be derived as follows:

Employing the reaction equation for the case where N is invariant with time, a simplifying assumption[3]

$$f(t) = 1 - e^{-\frac{\pi}{3}NG^3t^4} \qquad [8]$$

and substituting Eqs. 3 and 4 for N and G we have

$$\ln \frac{1}{t} = \ln K - \frac{3Q_G + Q_N}{4RT} \qquad [9]$$

for any given degree of recrystallization, for which a proper value of t is substituted; different values of t, however, affect only K and not the exponential; this equation is the same as Eq. 7, where

$$\frac{Q_R}{RT} = \frac{3Q_G + Q_N}{4RT}$$

The observed values of Q_R and the values of $\frac{3Q_G + Q_N}{4}$ taken from Table 5 are given in Table 6. The agreement is good for this sort of data.

TABLE 5.—*Values of Constants A, B, Q_N and Q_G for "Three-dimensional" Recrystallization*

Percentage of Elongation	A (5 Per Cent Recryst.), No. per Sec. per Sq. Cm.	Q_N, Calories	B, Cm. per Sec.	Q_G, Calories
5	2.7×10^{26}	78,000	5×10^{16}	59,500
10	3.6×10^{21}	61,000	2×10^{15}	57,000
15	6.5×10^{19}	53,500	6×10^{14}	55,000

TABLE 6.—*Comparison of Activation Energies Obtained by Different Methods*

Percentage of Elongation	Q_R, Calories	$\frac{3Q_G + Q_N}{4}$, Calories
5	64,500	64,100
10	59,600	58,000
15	52,100	54,600

INFLUENCE OF N AND G UPON THE FINAL GRAIN SIZE

One of the important features of nucleation and growth processes is the effect of the relative values of N and G upon the grain size of the completely reacted sample, the final grain size. It is evident, qualitatively, that an increase in the ratio of N to G will produce a decrease in final grain size, and conversely. This argument has long been used, especially in arguing the effect of the rate of cooling on the grain sizes produced on freezing, and in the present connection in explaining the effect of temperature, and especially of the degree of deformation, on the final recrystallized grain size—but no quantitative evidence has been advanced. Such evidence is available in the present data.

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* Baldwin[14] has used a similar equation to describe the effects of time and temperature on the softening of cold-drawn copper wire. Softening, however, does not always parallel recrystallization; 50 per cent softening does not necessarily mean 50 per cent recrystallization, but frequently means a lesser and uncertain degree of recrystallization.

The values of N, of G, and of the ratio of N to G, are plotted in Fig. 21, as functions of the degree of deformation. With increasing deformation, G appears to approach a maximum; some confirmation of this was obtained from measurements of G in 1-mm. sheets that had been cold-rolled to 90 per cent reduction in thickness, as given in Table 7. Comparison of the G values in material reduced 15 and 90 per cent show values that are nearly the same; indeed, at 308° and 310°C., for 15 and 90 per cent, respectively, the values are essentially identical, suggesting that G does not increase in this range. In such a circumstance, the steady decrease in final grain size with increasing deformation in high ranges of deformation must originate primarily in an increase in N with increasing deformation.

TABLE 7.—*Effect of Degree of Deformation on G, the Rate of Growth*

Temperature, Deg. C.	G, Rate of Growth, Cm. per Sec.	
	15 Per Cent Deformation	90 Per Cent Deformation
298		0.95×10^{-6}
308		1.35×10^{-6}
310	1.5×10^{-6}	
325	4.6×10^{-6}	$(8.6 \times 10^{-6})^a$

[a] Approximate value.

The effect of temperature upon the final grain size as observed in conventional recrystallization studies has been the subject of some controversy. The conventional recrystallization diagram usually shows a final grain size increasing with increasing recrystallization temperature.* However, investigations in which the as-recrystallized grain sizes in high-purity aluminum[15] and alpha brass[16,17] have been measured, show the final grain size to be essentially independent of temperature. Indeed, one investigation[18] on aluminum over a range of 0 to 10 per cent deformation showed a decrease in the final grain size with increasing temperatures.

Data on the final grain size in the studies of "three-dimensional" recrystallization are given in Table 8. Whereas the final grain size decreases with temperature in the samples elongated 5 per cent, and probably, though irregularly, in the samples elongated 10 per cent, this behavior is reversed in the samples elongated 15 per cent.

TABLE 8.—*Effects of Temperature and Deformation on Final Grain Size in 0.125-inch Recrystallized Sheets*

Temperature, Deg. C.	Grains per Sq. Cm.		
	5 Per Cent Elongation	10 Per Cent Elongation	15 Per Cent Elongation
310	145	345	
325	305	575	1330
350	400	530	1090
370	550	755	815

These behaviors should be reconcilable with the measured values of N and G. A direct comparison was not satisfactory, since experimental errors in the determination of N and G are large in relation to the small differences in grain size shown in Table 8. However, if values are read from the smoothed curves given in Figs. 19 and 20, a satisfactory comparison can be made. This shows that the ratio of N to G increases with temperature for 5 and 10 per cent elongation but decreases with temperature for 15 per cent deformation, in accordance with the observed final grain size.

This may be illustrated in another manner. If it is assumed that the number of grains is proportional to $\frac{N}{G}$, an approximate expression for the number of grains in the recrystallized grain structure can be obtained by substituting the temperature exponentials of N and G into this ratio, as follows:

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* It must be remembered that such diagrams, derived by the use of a constant annealing time, which at high temperatures is in excess of the time necessary for complete recrystallization, show final grain sizes determined not only by the interaction of N and G but also by grain growth (coalescence) following complete recrystallization.

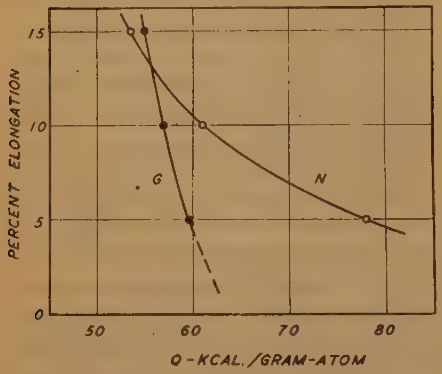

FIG. 23.—ACTIVATION ENERGIES FOR THREE-DIMENSIONAL NUCLEATION AND GROWTH VERSUS PERCENTAGE OF ELONGATION. LOT B ALUMINUM.

$$n \cong K \times e^{\frac{Q_G - Q_N}{RT}} \qquad [10]$$

where n is the number of grains, K is a constant, and the other quantities are as before.* Thus the number of grains will increase with temperature only when Q_N is greater than Q_G. As shown in Fig. 23, Q_N is greater than Q_G up to approximately 13 per cent elongation. At 15 per cent elongation, however, Q_G is greater than Q_N and the value of n should decrease with increasing temperature, as observed.

EFFECT OF INITIAL GRAIN SIZE

It is well known that strained single crystals recrystallize more reluctantly than strained polycrystalline aggregates at equal degrees of strain,[19] and it is known also that in polycrystalline aggregates the time for recrystallization is the greater the larger the initial grain size with equal strain, though quantitative data on this latter point are scanty. It has been shown that the critical degree of deformation for exaggerated final grain size[1] increases markedly with increasing grain size in iron[20] and in an aluminum alloy[21]; it has been observed that the softening temperature[1] in copper and iron[22] is the higher the larger the initial grain size, which points to the same effect. However, the effect of initial grain size ordinarily is considered as a variable of lesser importance in recrystallization behavior. There are no data on the effect of initial grain size in terms of N and G.

To provide more quantitative data on this point, and particularly to provide data in terms of N and G, a few preliminary experiments have been performed. Sheets 0.015 in. thick of lots C, D, and E, Table 1, were treated to give three initial grain sizes; namely, 484 grains per sq. mm., 345 grains per sq. mm. and 60 grains per sq. mm. These samples were elongated in tension to 5 per cent in the usual way and were then recrystallized at 350° and 400°C. The isothermal recrystallization curves, and the values of N and G, were determined.

TABLE 9.—*Effect of Initial Grain Size on G, the Rate of Growth, and on Final Grain Size of Samples Elongated 5 Per Cent*

Initial Grain Size, Grains per Sq. Mm.	Recryst. Temperature, Deg. C.	Rate of Growth, G, Cm. per Sec.	Final Grain Size, Grains per Sq. Cm.
484	350	2.0×10^{-5}	72
345	350	1.1×10^{-5}	78
60	350	1.7×10^{-6}	9
60	400	4.3×10^{-5}	19

The isothermal recrystallization curves, Figs. 24 and 25, show that the rate of recrystallization is the more rapid the smaller the initial grain size. This is to be expected. An additional experiment, with material with 8 grains per sq. mm., showed no evidence of recrystallization after 10 days at 350°C. when the experiment was discontinued.

The effect of initial grain size upon G is given in Table 9. Increasing the initial grain size from 484 grains per sq. mm. to 60 grains per sq. mm. has decreased G at 350°C. by a factor of 10.

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* The relation among N, G, and the final grain size may be expressed accurately for the case when N does not vary with time.[8]

A study of the effect of initial grain size on N produced unexpected results. It was observed that N *decreased* with time in the coarse-grained samples, as shown in Figs. 26 and 27. The observations are relatively few; the dashed lines represent a probable course of the N-t curves for the early stages of the recrystallization process. The fine-grained samples gave the usual exponential N-curves, and apparently the result is real and not due to experimental error. These results, which are purely preliminary, require and appear to deserve further study.

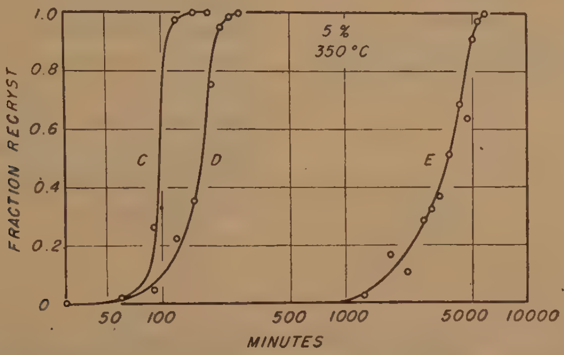

FIG. 24.—ISOTHERMAL RECRYSTALLIZATION CURVES FOR 0.015-INCH SHEETS OF ALUMINUM SHOWING EFFECTS OF INITIAL GRAIN SIZE.

C, 484 grains per sq. mm., D, 345 grains per sq. mm.; E, 60 grains per sq. mm.

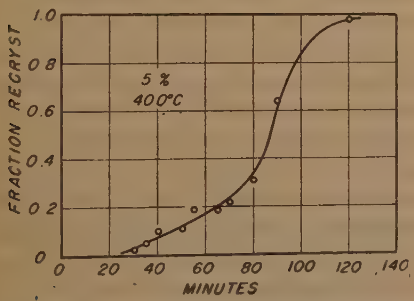

FIG. 25.—ISOTHERMAL RECRYSTALLIZATION CURVE FOR 0.015-INCH SHEETS ELONGATED 5 PER CENT AND RECRYSTALLIZED AT 400°C. LOT E ALUMINUM. 60 GRAINS PER SQUARE MILLIMETER.

EFFECT OF PRIOR RECOVERY

It has been observed that recovery at low temperatures prior to recrystallization in some metals, including commercial aluminum, retards the rate of subsequent recrystallization (see refs. 1 and 2 and references therein). The effect appears to lie in a decrease in N, with G unaffected.

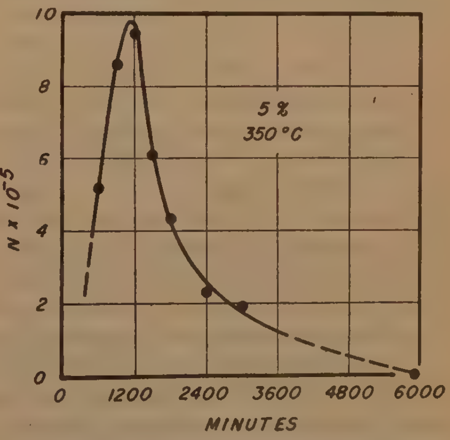

FIG. 26.—RATE OF NUCLEATION VERSUS TIME AT 350°C. LOT E ALUMINUM; 5 PER CENT ELONGATION. 60 GRAINS PER SQUARE MILLIMETER.

In the high-purity aluminum used here, however, a recovery treatment of 24 hr. at 250°C. following a 5 per cent elongation, in thin sheet of lot D, was found not in any way to affect subsequent recrystallization at 310° and 350°C.; this is in agreement with previous studies on high-purity aluminum.[15]

EFFECT OF HIGH DEGREES OF DEFORMATION

As stated earlier, the bulk of this study was necessarily limited to small ranges of deformation. In order to secure some idea, however qualitative, of how the N, and G, curves might behave in higher ranges of deformation, a few preliminary experiments were performed.

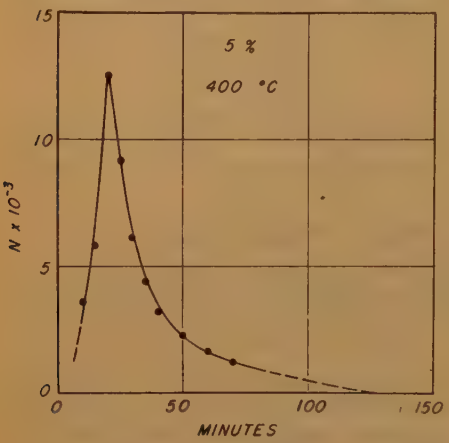

FIG. 27.—RATE OF NUCLEATION VERSUS TIME AT 400°C. LOT E ALUMINUM, 5 PER CENT ELONGATION. 60 GRAINS PER SQUARE MILLIMETER.

Sheets of lot A were cold-rolled 90 per cent reduction in thickness to 1 mm. and were recrystallized at several different temperatures, and the isothermal recrystallization curve was determined in the usual way. One such curve is given in Fig. 28. It is evident that the course of recrystallization is somewhat different, as compared with those for low degrees of deformation (compare Fig. 2), for the initial slow rate is nearly absent.

As noted in an earlier section, the value of G in these samples is not very different from that in samples strained up to 15 per cent; G is again observed to be independent of time. The difference between this curve and the type shown in Fig. 2, therefore, must lie in differences in nucleation behavior. An examination of the structure of the samples suggested that N varies with time in a manner similar to that exhibited in the recrystallization of coarse-grained material (Figs. 26 and 27), showing either a maximum in N at short times or steadily decreasing values of N from the beginning. This would explain the isothermal curve, Fig. 28. These results also are only preliminary and require further elaboration.

DISCUSSION

It is clear from the foregoing that recrystallization, proceeding by nucleation and growth, yields orthodox isothermal reaction curves. These curves show the effect of the recrystallization variables, such as temperature, degree of deformation, and original grain size on the rate of recrystallization; they show, as expected, that the rate of recrystallization increases with increasing temperature, increasing deformation, and decreasing original grain size. Such curves, which portray the time course of recrystallization, more accurately describe the recrystallization process than any conventional recrystallization diagram, which either ignores or inadequately depicts the effect of time. Any desired conventional diagram may be constructed from isothermal curves of this sort.

The determinations of N and G, yield the variations of these quantities with the chief variables. As expected, both N and G increase with temperature at all degrees of deformation. And, as expected also, N and G increase with the degree of deformation at all temperatures. The nature of this variation with deformation is of fundamental significance: N increases with deformation more rapidly than G; since the final grain size, after the completion of recrystallization, varies with the value of $\frac{N}{G}$, the final grain size decreases with increasing deformation, as has long been known.

It is useful to state this conversely: N decreases more rapidly than G with decreasing deformation, and as a result the final grain size becomes larger and larger as the percentage deformation decreases. At low deformation, a point will be reached where but one or a few nuclei will appear in the sample studied; since the rate of variation of N with deformation is large in this range, at slightly smaller deformations the probability of one nucleus forming in the sample studied in the time period chosen rapidly assumes very small values, indeed so small that it is exceedingly rare that any trace of recrystallization appears. Thus there should be a minimum deformation at which recrystallization appears, yielding large grains: this is the familiar "critical deformation for exaggerated grain growth."[1] If many samples, or one very large sample, were used, occasional evidence of recrystallization would be found at lower deformation, in accordance with the small but finite probability of nucleation. In view of the nature of this "critical" limit of deformation, it should not be sharp and precisely reproducible, and experience shows this. Moreover, the value of the "critical deformation" should decrease with increasing time of annealing, since nucleation is characterized by a time rate and increasing time increases the probability of the appearance of a nucleus.

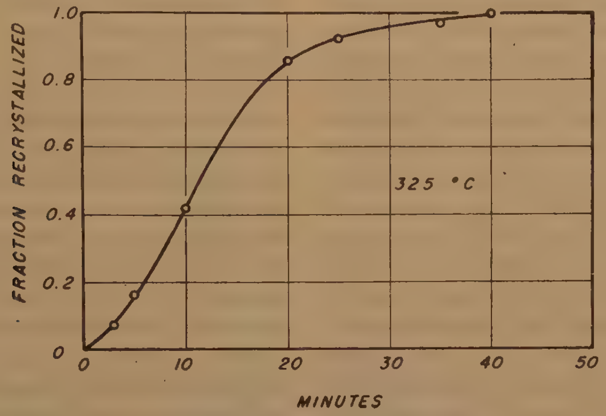

FIG. 28.—ISOTHERMAL RECRYSTALLIZATION CURVE FOR 1-MM. SHEETS OF LOT A ALUMINUM COLD-ROLLED 90 PER CENT.

In attempts to form single crystals by the strain-anneal method, it should be advantageous to anneal the strained sample so as to cause recrystallization at the lowest possible temperature, for the ratio $\frac{N}{G}$ is the lower, the lower the temperature, and thus the size of the resultant grain is the greater. Slow heating will provide this condition—and it has been found, in fact, that the frequency of success in the manufacture of single crystals is often greater with slow heating rates than with rapid heating rates.

The induction period, as it is represented in Fig. 7, appears to be a well-defined quantity. There has been much speculation concerning its nature.[2] Since nucleation is characterized by a time rate, each nucleus, apart perhaps from the very first, is initiated at some definite time period, and in this sense has an induction period; this, however, is but another way of saying that nuclei continue to form with time.*

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* Kornfeld appears to have adopted this view.[2]

The only question of fundamental importance is this: Does the first nucleus form at zero time? The question is difficult to answer, for the N versus time curve (Fig. 6) approaches the origin tangentially to the time axis: N at zero time is zero or nearly zero, and study of an extremely large sample would be necessary to answer the question. It seems much more reasonable to take the observed "induction periods" as proof that those nuclei formed at the time intercept itself. In this view, it would not be expected that the points on Fig. 7 would so accurately fall upon a straight line; in fact, Fig. 7 is somewhat unrepresentative in this respect, for usually the points are more irregular (compare ref. 2). The several points shown, derived from a series of samples, therefore represent nuclei that had formed at *about* the same time period, the appearance of which depends upon the probability of nucleation in the size of sample used; the "induction period" would thus be the smaller, the larger the sample. Rather than explaining the induction period, the problem appears to be to explain the nature of the variation of N with time.

The fact that the variations of both N and G with temperature are exponential in the manner shown indicates clearly that nucleation and growth in recrystallization are processes governed by activation energies. This has been proposed before, but the present plots are the most complete; earlier work failed to demonstrate this consistently.* The values of the activation energies Q_N and Q_G both change with increasing deformation in the manner to be expected; that is, they decrease.

The significance of Q_G is relatively simple: it represents the activation energy required to enable atoms in the distorted matrix at the interface of the growing recrystallized grain to move to and to become a part of the growing grain. Since these atoms are at various energy—i.e., stress levels—the value of Q_G is an average for all atoms. Atoms at high energy levels attach themselves quickly (at this microscopic point G is high); but as material at this energy level is consumed, growth must continue by absorption of atoms at lower stress levels (where G is low); thus G should show a fine structure, on the scale of the microscopic stress contours. Microscopic observation confirms this qualitatively, for it is observed that the growing grain grows more rapidly at the matrix grain boundaries, where presumably the energy is highest; and it is observed also that the advancing front of the recrystallized grain is farther ahead (G is greater) in some matrix grains than in others, in conformity with the heterogeneous nature of the straining among the different crystals in an aggregate. The value of G measured, therefore, must be related to the average energy of the strained matrix. With increasing deformation the average energy increases, and the necessary activation energy decreases, as shown by the decreasing Q_G value.

Although there has been some controversy on the point, it is usually assumed that nuclei form at points of highest energy.[6,7,19]* Whether nuclei form at points of highest energy or at points of lowest energy (as some have claimed) cannot now be decided by direct experiment,† and at the moment the answer must result from argument. Microscopically, in single crystals or in aggregates, it is observed that nuclei form preferentially at slip lines, grain boundaries, and twin bands; i.e., at points where there is good reason to suspect high stress levels.

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* See Kornfeld, references in ref. 2 and Karnop and Sachs.[23]

* It is thought that these points of high energy represent points of maximum lattice curvature; this is assumed in order to explain the fact that reversed deformation decreases N; see references in ref. 19.

† The new technique described in the Institute of Metals Lecture for 1945, by C. S. Barrett, may be useful here. (See p. 15.)

In addition, the fact that N increases with increasing deformation argues for nuclei at high stress points, for the number of such points must increase with increasing deformation. Furthermore, the fact that simple activation plots of N versus temperature yield orthodox activation energies, argues in the same way, for the high stress points should become increasingly active with increase in temperature as the energy of the lattice increases with temperature; in a word, the high-stress-point theory appears capable of explaining the temperature coefficient of N, where the low-stress-point theory gives no hint of an expected temperature coefficient without recourse to theories of such complexity that they are objectionable. Moreover, the fact that when prior recovery affects the rate of recrystallization the effect is found to be restricted to a decrease in N and G unaffected,[2] high stress points should respond more quickly to recovery treatments, and this argues for the theory of high stress points. Finally, the fact that Q_G is doubtless associated with the average energy of the deformed metal, and the fact that Q_N decreases more rapidly with deformation than Q_G, argues that the activation energy Q_N (and thus nucleation) is associated with high energy points, for these could reach very high values as compared with the increase in average energy.

The observed variation of N with time, however, is a difficulty on any theory. On the high-stress-point theory it would be expected that N should decrease with time as the high stress points are consumed. The observed curve appears autocatalytic in nature; such an autoacceleration would appear to argue for an action at a distance; that is, that the occurrence and growth of one nucleus should transmit through the unrecrystallized matrix an accelerating stimulus to nucleation.[2] Such a stimulus necessarily would be in the nature of a deformation. This has been advanced in explanation of a like effect in nucleation of pearlite from austenite.[4] But in recrystallization the volume change is very slight and hardly seems adequate. This problem remains a difficult one.*

The Becker[7] theory of the rate of nucleation in recrystallization, derived by analogy with polyphase nucleation[9] and representing the most complete theory at the moment, is not supported by this work. Becker's expression for N is as follows, in abbreviated form, combining constants:

$$N = K \times e^{-\frac{K^1}{\delta^2} \times \frac{T_s^2}{T(T_s - T)^2}}$$

where K and K' are constants, T is the absolute temperature, T_s the absolute melting temperature, and δ is the deformation expressed as the decrease in heat of sublimation (the increase in internal energy in cold-work). It is not possible to test this equation with respect to δ, for the relationship between δ and the elongation is not known. However, the expression yields the wrong temperature coefficient of N, for as T decreases from T_s, N increases, passing through a maximum at $T = \frac{1}{3}T_s$, thence decreasing toward lower temperatures. The observations show a simple activation decrease in N with temperature decrease in the temperature range studied ($T = \frac{2}{3}T_s$). Nucleation theory is much in need of further development, and such development must not only predict the correct temperature coefficients but also the observed variation of N with time.

SUMMARY

1. *a*. Measurements have been made of the recrystallization of cold-worked

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* The decomposition of barium azide shows similar N versus time curves.[24] It is hardly conceivable that a similar variation should be observed in condensation and freezing, though apparently the point has not been studied; if this were found, the effect would then be recognized as a fundamental characteristic of the nucleation process and special explanation for solid-solid reactions would be unnecessary.

high-purity aluminum in sheet 0.015 in. thick in terms of isothermal recrystallization-rate curves, and in terms of the rate of nucleation N, and the rate of growth G, over a temperature range of 280°–400°C. and a range of deformation by elongation in tension from 0–15 per cent. The isothermal curve may be calculated from the values of N and G. In these thin sheets the recrystallized grain size is greater than the sheet thickness, introducing special features into the recrystallization process; such recrystallization is termed "two-dimensional" recrystallization.

b. It was found that N increases with time up to 30 to 40 per cent recrystallization; G is invariant with time. Both N and G were found to increase exponentially with temperature. Both increase with increasing deformation, but N increases more rapidly than G, accounting for the smaller final recrystallized grain size after high degrees of deformation. The effect of temperature upon the recrystallized grain size results from the change in the relative values of N and G with temperature.

c. Measurements are reported on the "induction period" as a function of temperature and percentage deformation.

d. Activation energies have been calculated from the temperature coefficient of N and G; both Q_N (nucleation) and Q_G (growth) decrease with increasing deformation, but Q_N decreases more rapidly than Q_G.

2. *a*. Similar studies were made, with similar results, for the recrystallization of thick sheets, 0.125 in. in thickness. In these the recrystallized grain size is much smaller than the sheet thickness; such recrystallization is termed "three-dimensional" recrystallization.

b. The thick (0.125 in.) sheet studied recrystallized less rapidly than the thin (0.015 in.) sheet, owing apparently to an originally higher degree of preferred orientation in the thin sheet. Thus the degree of preferred orientation is a variable affecting recrystallization behavior. The problem of the quantitative relationship between "two-dimensional" and "three-dimensional" recrystallization is explored, and methods of interconversion are proposed. The thickness of the sheet is a variable affecting recrystallization behavior, owing to the restrictive effect of sheet thinness on nucleation.

3. The rate of recrystallization increases markedly with decrease in the initial grain size, as shown by isothermal curves and by measurements of N and G. In coarse-grained material N was observed to decrease with time.

4. Studies were made at high degrees of deformation, 90 per cent by cold-rolling, which suggest that N initially increases with time, passes through a maximum and then decreases. These studies show that N steadily increases with deformation, but that G reaches a limiting value at about 15 per cent deformation and thence onward changes but little.

5. The observed behavior of N and G have been employed to provide a basis for recrystallization behavior as represented on conventional recrystallization diagrams, and have been used also in discussing the theory of recrystallization. The evidence is good that recrystallization nuclei form at points of high stress.

Acknowledgments

The authors wish to express their appreciation to the Aluminum Company of America for granting a fellowship to one of them. They wish also to acknowledge with thanks the assistance in the experimental work of Mr. Charles A. Adams and Mr. William Carpenter, who made many of the early measurements, and also of Mrs. Edna Matson, who assisted in the latter part of the work.

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DISCUSSION

W. M. Baldwin, Jr.*—In describing the isothermal recrystallization curve for aluminum given in Fig. 2, the authors say that this curve is general among metals, the same type of curve being obtained in the recrystallization of silicon ferrite and the pearlite-austenite transformation. To these examples might be added the case of the recrystallization curve for severely cold-rolled copper strip. In a recent article on the annealing of copper strip at room temperature,[25] Dr. Cook presents 12 micrographs showing the progressive development of recrystallized material. The reaction takes place over a period of months and is completed in something over a year.

The writer has taken the liberty of constructing a plot of the variation of recrystallized material appearing in Dr. Cook's micrographs as a function of time. It is realized that the data are not highly accurate, since the values recorded refer only to the areas included by the micrographs and are not an average of the samples as a whole. Nevertheless, they do conform to the type of curve expected for general nucleation. Unfortunately, Dr. Cook did not employ an etchant (such as aqueous ammonium persulphate solution) that would reveal the individual grains, thus permitting some rough estimate of the rate of nucleation and rate of growth. Despite the long time intervals involved in this recrystallization study, it is recommended that Dr. Cook's experiments be repeated for the specific purpose of studying recrystallization rates.

Such a study would be interesting for a number of reasons: (1) The isothermal curves would be conducted in temperature ranges where suitably chosen boiling liquids could be employed for heat baths, thus permitting a high degree of accuracy with regard to temperature control; (2) the recrystallization reaction would take place between a specific starting and final orientation; and (3) some idea of the cause of the elliptical shape of the grains, typical to this annealed texture, might be gained. With regard to the last point, it is quite probable that there is a certain amount of directionality in the disposition of nucleation points as well as in the rate of growth.

C. G. Dunn.*—It was stated by the authors that any theory of nucleation, including the high-stress-point theory, runs into difficulty because it is observed that N increases with time. I should like to ask why this theory should predict a decrease of N with time, in view of the fact that one might expect to find more stress points of somewhat lower stress value than the highest ones, which presumably start the recrystallization process after the induction period has been attained? In this connection, the data shown in Fig. 4 indicate that higher degrees of deformation, and therefore presumably higher degrees of stress, lower the induction period—another way of stating that the highest stress points (of fewer numbers, presumably) start the transformation.

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[25] *Jnl.* Inst. Metals (1944) **70**, 159.

* Research Physicist, General Electric Co., Pittsfield, Massachusetts.

It was also stated by the authors that neither aluminum nor silicon ferrite form annealing twins. This may be true for fine-grained samples, but it is not true for large-grained material of silicon ferrite, because it has been shown[26] that annealing twins, involving in some cases more than one order of twins, can be formed readily in such materials by cold-rolling a small amount and annealing above the recrystallization temperature.

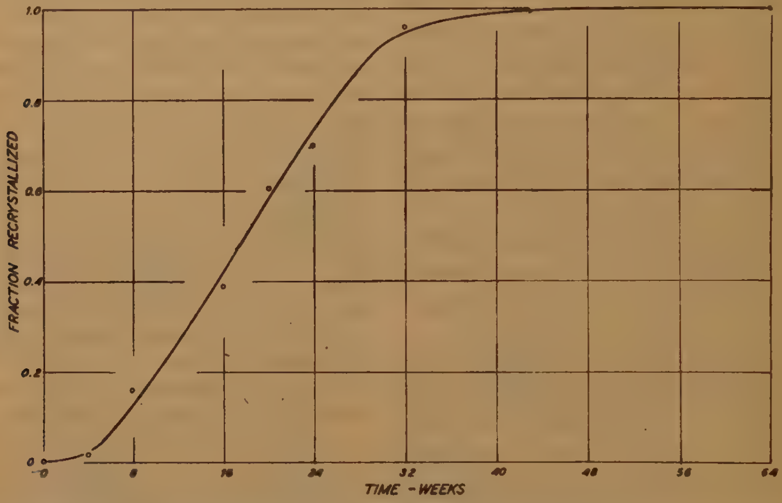

FIG. 29.—ISOTHERMAL RECRYSTALLIZATION CURVE FOR COPPER STRIP COLD-ROLLED 97.5 PER CENT. ROOM-TEMPERATURE ANNEAL. (*Cook and Richards.*)

L. W. EASTWOOD.*—It is stated in this paper that G is independent of time. This is a bit difficult to understand, as it has been my observation that G decreases as recrystallization approaches completeness unless the temperature is high, and considerable coalescence occurs after recrystallization is complete. Only the smaller, younger crystals grow, and the larger ones discontinue growing as the equilibrium grain size is reached. Indeed, if this were not so, and grain growth did not slow down and cease at equilibrium grain size, the piece would soon be composed of a few very large grains. This is well illustrated by the authors' Fig. 1. After 60 hr., Fig. 1*c*, and certainly after 70 hr., Fig. 1*d*, the maximum grain size when recrystallization is about ¼ to ½ complete is as large as when recrystallization is complete at the end of 100 hr., Fig. 1*f*.

Second, as shown by the slope of the curve, Fig. 5, N must also approach zero as recrystallization becomes complete. It follows, therefore, that the N values may not increase exponentially and G remain constant throughout the recrystallization process.

Third, why should G increase with increasing deformation? One would expect G to be a function of temperature only. This can be easily demonstrated by causing recrystallization to occur in a bar having a gradual strain gradient. If this is done, probably it would be found that the grain size at various degrees of deformation is about the same, providing recrystallization is just complete or less than complete and the grains were initiated about the same time. Since the incubation period is longer the lower the degree of deformation, the newest grains formed at low degrees of deformation will be the smallest, of course. If G increased with the degree of deformation, the average grain size in the strain-gradient bar should increase with increasing deformation up to where recrystallization is complete. However, I do not believe that this is true.

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[26] C. G. Dunn: Recrystallization and Twin Relationships in Silicon Ferrite. *Trans.* A.I.M.E. (1944) 158, 372–386.

* Assistant Supervisor, Battelle Memorial Institute, Columbus, Ohio.

Fourth, there is a question in respect to the significance of the difference in Q_G and Q_N values. Experimentally, the authors apparently have established a difference. The question is, when does a nucleus become a recrystallized grain and the energy of activation pass from Q_N to Q_G? Actually, the authors show that the values of Q_G and Q_N are of the same order of magnitude. Are not Q_G and Q_N actually the same value and the differences shown in Table 3 well within experimental error? If the authors are convinced there is a difference in Q_G and Q_N values, I should like their opinions on the cause of this difference. If Q_G and Q_N are the same, the grain size of the just recrystallized material would be independent of temperature. If Q_N and Q_G are different, and have slightly different temperature coefficients, the just recrystallized grain size would be correspondingly different, depending upon the temperature of the recrystallization treatment.

Presumably, the authors' conclusions are based on more precise measurements of N and G values than previous data. Presumably also, they have based their conclusions on a considerable amount of data not shown in the paper.

J. K. Stanley.*—It is indeed heartening to find that the recrystallization results obtained some time ago on silicon ferrite[2] have been substantiated on aluminum. The same general shape of the isothermal recrystallization curve was found; the rate of nucleation was found to increase with time; and the apparent constant rate of growth was also noted.

There are of course numerous difficulties in the knowledge of recrystallization in this type of studies. One of these problems that has concerned the writer is the rate of growth; is it actually constant or is it apparently constant because of the nature of its evaluation? In our studies of growth, we have been assuming that the largest grains were nucleated at the first instant of reaction and that all of the largest grains were nucleated at the same time. We have not been able to check this assumption experimentally. It is conceivable that the rate of growth is not constant, and it may be because of this that there is the discrepancy between the calculated and experimental isothermal recrystallization curve. That the rate is not constant appears to be borne out by the following calculation.

Using Eq. 5 of the paper and solving for the rate of growth G, using the parameters of nucleation given in Table 2, it appears that the rate of growth is not a constant. For material deformed 5.1 per cent by elongation and recrystallized at 350° the following results are obtained:

Time, Sec.	$f(t)$	Rate of Growth G, Cm. per Sec.
3,000	0.003	0.7×10^{-5}
4,000	0.025	1.1
5,000	0.14	1.7
6,000	0.38	2.0
7,000	0.65	2.1
8,000	0.88	2.2

Only the first four figures for G need concern us, because the exponential nucleation equation does not hold for $f(t)$ greater than about 0.4. It is evident that the rate of growth is not constant but increases somewhat with time.

In discussing the microscopic aspects of growth, the authors say that the "advancing front of the recrystallized grain is farther ahead (G is greater) in some matrix grains than in others, in conformity with the heterogeneous nature of straining among different crystals in the aggregate." Is this actually the case or could such growth be due to the effect of orientation where matrix grains of orientations similar to the orientation of the nucleus are adsorbed more rapidly by the growing nucleus than less favorably oriented grains?

In the discussion of the high stress theory, the authors use a preliminary result of the original work on silicon ferrite to support their high-stress theory. The observation made earlier, that room-temperature recovery appeared to decrease the nucleation, has not been substantiated in a more detailed study.[27] Actually, recovery of cold-worked silicon ferrite at 350° appears to increase the nucleation slightly when the material is recrystallized. This is contrary to the high-stress theory as presented in the paper. More work is necessary to definitely establish the effect of recovery before such data can be safely used to support a theory.

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[27] J. K. Stanley: Effect of Variables on the Recrystallization of Silicon Ferrite in Terms of Rates of Nucleation and Growth. *Trans.* A.I.M.E. (1945) 162.

W. A. Anderson and R. F. Mehl (authors' reply).—The process of recrystallization is important, the phenomena are many and complex, and the theory not readily apprehended; much careful thought is required.

We were aware of Dr. Cook's very interesting paper; the isothermal curve which Dr. Baldwin has drawn from the published micrographs is, as he says, orthodox, despite the fact that Dr. Cook did not intend that his micrographs should accurately represent the average degrees of recrystallization. A similar isothermal recrystallization curve for copper has been published by Sauerwald and Globig.[28] The plan of study Dr. Baldwin proposes is interesting; it suffers, as he realizes, from a restriction to low temperatures, whereas in practice recrystallization is performed at higher temperatures. There is, in fact, a program underway in this laboratory, by Dr. Wang, for a detailed study of recrystallization of copper and copper-base alloys, in an effort to obtain quantitative measurements on the effect of solid solution formation on N and G. There are no data of this type so far reported. Some experimental difficulties are encountered: grain-size changes occur during preliminary treatments, owing to the intrusion of internal oxidation; the early recognition of recrystallized grains in lightly worked samples exhibiting a profusion of annealing twins is difficult.

We agree that a study of recrystallization in terms of N and G as affected by preferred orientations is needed. In the rather limited ranges of cold-work studied here, no evidence for a directionality in the alignment of nuclei was observed; the text recounts our observations on the apparent effect of preferred orientations on G.

Dr. Dunn reasons that the rate of nucleation should increase with time if the number of stress peaks and their "induction periods" increase as their stress values decrease. This reasoning is correct providing one can justify the assumption that each stress peak has a definite and fixed induction period for nucleation; that is, a definite and fixed time when it becomes a nucleus, a time that is longer the lower the stress. On the basis of the high-stress-point theory of nucleation, however, it would be expected that nucleation would be governed by probability, with points at various stress levels contributing finite numbers of nuclei. It can be reasoned that the probability of nucleation at a point of stress, and therefore the fraction of the high stress points that actually nucleate, will be greater the higher their stress. This probability, summed over all values of stress in a unit volume of unrecrystallized matrix, will determine the rate of nucleation at any time. Since the proportion of points at high stress will decrease more rapidly through nucleation than points of low stress, there should be a decrease in the total probability of nucleation in the unrecrystallized matrix, and accordingly a decrease in the rate of nucleation, as recrystallization progresses. Dr. Dunn's ideas on this subject are similar to those we have entertained from time to time, but thus far we have been unable to employ them satisfactorily to account for the form of the $N - t$ curve. The physical theory of nucleation in solid-solid reactions requires attention, as we have said in other connections elsewhere.

As to annealing twins—we have, of course, made no study here of twin relationships. Our comment on this point is restricted to the obvious fact that the essential absence of true annealing twins in fine-grained aluminum and silicon ferrite is favorable to the early recognition, measurement, and counting of the recrystallized grain (see reply to Dr. Baldwin above).

We find ourselves in disagreement on several counts with Dr. Eastwood. It is possible that this originates in a difference in point of view, for Dr. Eastwood appears at times to be discussing coalescence following the completion of recrystallization, or following substantial impingement of growing grains, whereas the measurements reported in the text on N and G were made in such a way to be free of any effects of coalescence—the new recrystallized grains were measured before impingement with other growing grains, as stated in the text. It is important that the phenomena of recrystallization be distinguished as separate from those of coalescence following the completion of recrystallization, for these are in fact wholly separate and different types of process.

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[28] Sauerwald and Globig: *Ztsch. Metallkunde* (1938) 25, 33.

Thus in Dr. Eastwood's second paragraph, he is obviously not considering G as a rate pertaining only to the growth of a recrystallized grain into an unrecrystallized matrix, as we have, but is considering also changes, or lack of changes in grain size after impingement. The fact that the final recrystallized piece does not show "a few large grains" is brought about by impingement of the grains that nucleate early with other growing grains. In arguing grain size in recrystallized materials from values of N and G, impingement must be considered. To neglect it confuses the whole problem. Accordingly Dr. Eastwood's arguments from Fig. 1 do not pertain to our observation, based on measurement, that G is invariant with time. We should also point out that our measurements were made on aluminum; our conclusions obviously apply only to aluminum and do not apply to any other metal. Indeed measurements have been reported that G in the recrystallization of tin decreases with time (see references quoted in ref. 2).

As to the third paragraph, reading of the text will disclose that we believe that the exponential relationship observed for the early part of the $N - t$ curves is not maintained in the latter stages, and we have shown some evidence that N decreases in the latter stages. Owing to the extreme difficulties in measuring N in the latter stages (see text), we have not been able to provide good data for these stages. As to G, there is no evidence, directly or indirectly, that G varies during recrystallization in high-purity aluminum; all of the measurements reported here show an independence of time (see references quoted in ref. 2).

As to the fourth paragraph, we cannot follow the argument. It assumes an experiment that shows an independence of the final grain size upon the prior degree of deformation. We know of no case where this obtains; in all reported cases the final grain size is the greater the lower the degree of prior cold-work, to the point of critical strain for large grains (see ref. 7, Fig. 7). This is in fact true for a gradient-strained bar of copper, the experiment suggested (Karnop and Sachs, ref. 23); and is true also for the cases previously investigated by Dr. Eastwood (refs. 15 and 16). It is one of the laws of recrystallization. Even if the result should be as Dr. Eastwood postulates, and if the variation of N with degree of prior deformation is admitted, then necessarily G must vary also. The value of G alone does not determine the final grain size—that is the result of the ratio of N and G. It is important to note that the variation of G with prior deformation is experimentally demonstrated in the text—it is not an assumption, but a fact.

As to the fifth paragraph, it is not easy to devise theories of the energy of activation of nucleation and of that of growth. There seems to be sufficient difference in the physical natures of the two processes to predict a difference between Q_N and Q_G (see Stranski's theoretical work, ref. 23 quoted in ref. 4). It is true that a difference between Q_N and Q_G means a difference in the final grain size after recrystallization at different temperatures—this is stated in the paper and is not a new thought.

The conclusions are based only on the data shown in the text. It is not good science to base conclusions on unquoted data. It might be interesting and informative to other workers to note here the amount of labor involved in such work as this. The rate of nucleation is determined by the actual measurement of the sizes of each of the individual grains in a series of samples. To obtain all of the data given in the text on N required 35,000 separate measurements of individual grain diameters. The rate of growth is determined by measurement of the diameter of the largest grains in each of a series of samples. The data given on G required 1600 such measurements.

Mr. Stanley's conclusion that the value of G in aluminum increases with time is based on the assumption that the true rate of growth can be calculated from Eq. 5 if the degree of recrystallization and the value of N are known at any time. Ideally, this assumption is correct; however, in applying Eq. 5 in this way it must be borne in mind that the values of the rate of nucleation are subject to some experimental error and that this error will then appear in calculated values of G. This is clearly shown when Mr. Stanley's calculations are extended to all of the data in the present investigation; it is then found that the calculated values of G do not invariably increase with time but often decrease, or remain constant.

Mr. Stanley is correct in pointing out that preferred orientations may play a part in determining the rate of growth in individual grains of the strained matrix. Actually, our knowledge of the effects of preferred orientations on the rate of growth is meager and they may or may not be a factor of importance (see reply to Dr. Baldwin above).

In discussing the effects of prior recovery on *N* and *G* we were referring particularly to the work of Kornfeld and Pawlow [*Phys. Ztsch. Sowjetunion* (1934) 6] discussed in ref 2. These investigators found that *G* is unaffected by prior recovery but that the number of recrystallized grains and the incubation period were decreased. The decrease in the number of grains could result only from a decrease in *N*. We agree with Mr. Stanley that further investigational work is necessary before a complete understanding of the effects of recovery can be had.

Textures, Anisotropy and Earing Behavior of Brass

By F. H. Wilson* and R. M. Brick,† Members A.I.M.E.

(New York Meeting, February 1945)

With the papers of Palmer and Smith[1] and of Burghoff and Bohlen,[2] published in 1942, understanding of the problem of the development of ears on deep-drawn brass cups was brought to the point where, from a practical standpoint, producers of brass sheet could keep earing under control. However, these very practical results raised questions concerning the reasons for the observed behavior. Since plastic deformation is fundamentally a function of crystallographic slip, these reasons must be considered in the light of the textures to be found in the annealed sheet.

Various attempts have been made to interpret the mechanism of ear formation by correlation with the preferred orientation and the anisotropy of the sheet. However, none of these has satisfactorily explained why ears are usually found in the rolling and transverse directions for copper but at 45° to these directions for brass. This paper offers additional data on these two related subjects and has been divided into two sections. The first section provides a survey of the recrystallization textures of brass as affected by annealing temperatures and prior reductions, and an account of the earing behavior which accompanies these textures. The second section reports new data on the anisotropy that accompanies a characteristic texture for brass and endeavors with partial success to establish the factors that account for the difference in earing behavior between copper and brass

Earing Behavior of Brass

Review of Textures

The recrystallization texture of severely rolled brass was first reported by Bass and Glocker.[3] The preferred orientation to which this texture, obtained from metal annealed at 500°C., was most akin was (113)[112]. This texture has been confirmed by Bauer, von Göler and Sachs;[4] Brick;[5] Brick, Martin and Angier;[6] and Cook and Richards[7] who, in general, used annealing temperatures under 500°C.

Bass and Glocker[3] also reported the recrystallization texture at 850°C. to be the same as at 500°C. They analyzed their textures by means of single photograms obtained with white radiation. The photograms for both temperatures are reproduced in their paper, and there is a strong similarity between the two. However, for the latter temperature, the number of spots registered on the film was remarkably large for the grain size to be expected, and the authors made no mention of using a technique that would integrate a large enough area of the specimen to produce so many spots.

The only other attempt to determine textures resulting from high temperature

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[1] References are at the end of the paper.

anneals in brass is that by Burghoff and Bohlen.[2] Two pole figures were presented for materials that were given final anneals at 1200°F.(650°C.) with different prior histories. The textures are conspicuously different from the previously reported (113)[112] recrystallization texture. The authors felt that these pole figures could best be described as two different distributions around the (110)[112] orientation. Other data from this paper, and from that of Palmer and Smith, indicate that considerably greater variation in texture might be expected from modifications in the mill practice. It is evident that the common report that the recrystallization texture of brass is (113)[112] needs further clarification.

It should be stated here that Cook and Richards[7] used the Burghoff and Bohlen pole figures to reach the conclusion that the recrystallization texture of brass rolled 50 to 80 per cent was similar to the rolling texture. It will be seen, on the basis of the present research, that the degree of rolling had only a minor role in the development of these textures, the temperature of final anneal being significant. This X-ray diffraction study of the effect of final annealing temperature was made possible by construction of a structure integrating camera for determining preferred orientations in large-grained specimens.

Review of Earing Behavior

Ears on brass cups have generally been assumed to occur only at 45° from the rolling direction. Cook, in reply to discussion of his paper on Directional Properties in Rolled Brass Strip,[9] reported observance of ears at 0° and 60° from the rolling direction. Burghoff and Bohlen[2] and Palmer and Smith[1] also found that ears on brass cups can be made to occur in these positions. The pole figures of Burghoff and Bohlen were for materials that gave four ears at 45° and six ears at 60°. Palmer and Smith found that this six-ear form occurred only if the ready-to-finish anneal is high, such as 650°C.

A different form of cup contour seems to have been found by Phillips and Samans, as reported in their discussion of the Burghoff and Bohlen paper[2] and by Cook and Richards.[7] Phillips and Samans reported the ears to be at 52° from the rolling direction, and Cook and Richards at 55° from the rolling direction. This form seems to develop following reductions of 90 per cent or more.

It has been pretty well established[1,2,7,9] that the height of ears in brass increases with the temperature of final anneal, decreases with the temperature of ready-to-finish anneal, and, in general, increases with the amount of reduction. Palmer and Smith[1] found that very high ears, occurring at 45°, could be developed by alternately rolling 4 to 6 B. and S. numbers and annealing at 350° to 450°C., particularly when the final annealing temperature was high.

Since the earing behavior is an indication of the recrystallization textures, a plot such as is given in Fig. 1 (reproduced from Palmer and Smith) suggests that considerable variation in textures might be expected from modifications in mill practice. For instance, if the final anneal is at 650°C., a lessening of ear height occurs for reductions between about 12 and 20 B. and S.* numbers, which is not found if the final anneal is 500°C. Six-ear forms are found between 16 and 22 B. and S. numbers in material that is given a 650°C. ready-to-finish anneal, but not when the ready-to-finish anneal is 500°C. The first observation implies that for 12 to 20 B. and S. numbers reduction, variation in texture will result from variation in temperature of final anneal. The second observation implies a difference in final recrystallization texture between materials rolled from fine-grained and coarse-grained bars. The former implication has been confirmed in the present research. However, no work has been done on brass rolled from originally fine-grained stock, and confirmation of the latter must be left until this is done.

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* The reductions in this paper, as in Palmer and Smith's, are expressed in terms of B and S gauges, since this logarithmic scale is a more significant indicator of the high deformations affecting textures. For example, the difference between a 20 and a 30 B and S numbers reduction may considerably affect orientations although expressed in the usual manner, the corresponding figures of 90.4 and 96.9 per cent reductions do not appear to differ greatly.

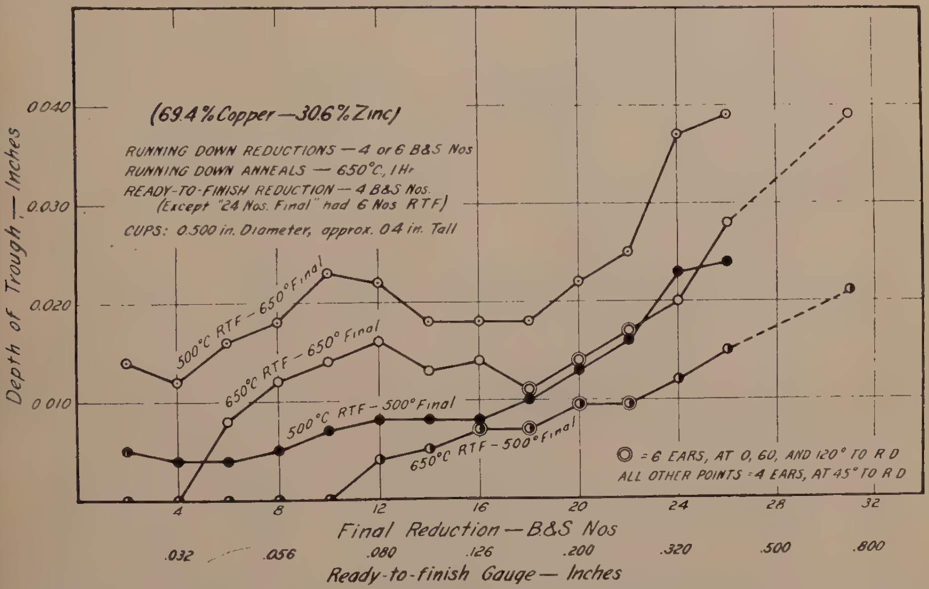

FIG. 1.—SOME VARIATIONS IN THE EARING BEHAVIOR OF BRASS THAT SUGGEST VARIABILITY IN ANNEALING TEXTURES. (*Palmer and Smith.*[1])

The increase in ear height with temperature of final anneal is probably not attributable to increase in grain size alone. A determination of the extent to which the type and degree of perfection of the preferred orientations found at higher final annealing temperatures contributes to increased ear height was one objective of this research.

The interpretation of the mechanism of earing has never been satisfactorily accomplished. Frequently explanations have gone no deeper than to indicate that ears are found in the directions of maximum elongation or minimum tensile strength. These directional properties have rarely been related to crystallographic texture. The "maximum elongation" interpretation could be a rather satisfactory one if it were not for the fact that ears on cups drawn from sheet metal having a (100)[001] texture occur in the directions of minimum elongation.

Cook and Richards[8] have made the first serious attempt at correlating anisotropy and earing behavior of "cubic" copper with texture by introducing calculations of resolved shear stress on the active slip planes for different directions of application of total tensile stress. Their attempt suffers from failure to take into account the presence of large circumferential compressive stresses in the blank of the cup (see p. 20), and from using "ultimate breaking stress" as measured for each direction as the total applied force for determining resolved shear stress. Their attempt to make the calculations fit the observed behavior has led to some questionable conclusions.

The results of some new approaches to this problem are included in this paper with the hope that the data can be of some value when the final interpretation is achieved.

Materials and Methods

The material used in this research was a good quality of cartridge brass of the following composition: copper, 70.70 per cent; zinc (by difference), 29.39; lead, 0.006; iron, 0.003. This material was rolled in the mill from a 2½-in. casting to 1.080 in., annealed, rolled to 0.440 in., annealed and milled to 0.400 in. From this gauge, various rolling and annealing schedules were completed in the laboratory.

For determining the texture, photograms were taken at nine different angular positions of beam to specimen. Photograms in additional positions were taken for confirmation of questionable areas of the pole figure. Unfiltered CuK radiation was used, giving a θ angle of 21° 30′. Only the (111) ring was read and all pole figures are octahedral pole figures. In plotting the pole figures, four degrees of intensity were estimated visually and recorded on tracing paper over a pole figure chart.

The camera, which was constructed for this research, was designed to permit coverage of a 1½ by 3-cm. specimen area, large enough to give continuous rings from material having a grain size of 0.120 mm. The motion of the specimen was such that the X-ray beam traversed a horizontal path across the specimen and back at 60 different levels, which were ½ mm. apart. Since a pinhole of 1-mm. diameter was used, overlapping of the paths of the beam occurred. Motor speed and gear reduction were such that 16 min. was required for a complete revolution of the lifting cam, during which time the area of the specimen was covered four times. Rotation of the specimen around a vertical axis through the point of contact of the beam and specimen was possible up to 67° from the normal position.

No satisfactory method for eliminating the problem of intensity differences due to absorption in the specimen was found. It was therefore necessary to take this known effect into account when estimating intensities. It is felt that, although the exact extent of the areas within the pole figures that are assigned primary, secondary, or tertiary intensities may be open to question, the positions of these areas, which are more significant in determining type of texture, have been accurately determined. However, allowance should be made for these variables whenever two pole figures are compared for relative perfection of texture.

Since the purpose of the research was to determine what light could be thrown on the earing characteristics of brass by determination of the preferred orientations, an endeavor was made to draw cups from the same material for which pole figures were made. From all material that was finished at 0.020-in. gauge, ½-in. dia. cups were drawn. The contours of the rims of the cups were measured and have been plotted around the pole figures, each shading line representing 0.010 inch.

Texture Changes with Increasing Deformation

The effect of increased cold-rolling on the deformation texture and the textures after annealing at 400° and 700°C. was determined for the 70-30 brass. Other investigators[6,7] have reported that the deformation texture and the low-temperature recrystallization texture follow a steady progression of increasing perfection with increasing deformation above about 50 per cent reduction. Present results confirm this, and since they have not been previously presented in the literature, pole figures showing the increasing perfection are herein reported.

Material for this series was annealed for 2 hr. at 700°C. at the 0.400-in. gauge. It was given processing reductions of 4 to 6

B. and S. numbers and processing anneals of ½ hr. at 650°C. to bring it to the gauge desired for the final reduction. This final reduction was from such a gauge as to produce a final gauge of 0.020 in. with the desired deformation. The processing schedules for all of the specimens are given in Table 1.

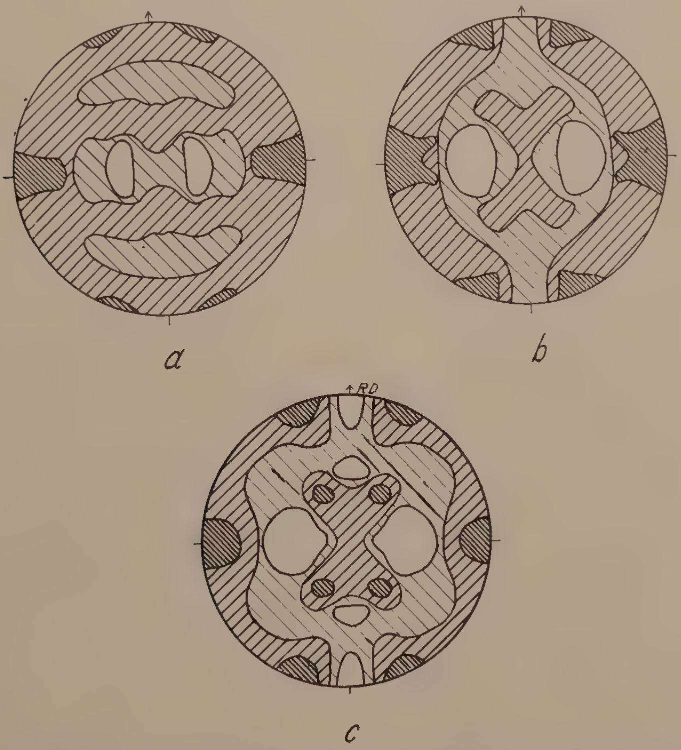

FIG. 2.—DEFORMATION TEXTURES OF 70-30 BRASS FOLLOWING INCREASING REDUCTIONS.
Rolled, B. and S. numbers: (*a*) 8; (*b*) 20; (*c*) 34. (Octahedral pole figures, rolling direction vertical.)

TABLE 1.—*Production Schedules*

Final Reduction, B. and S. Numbers	Processing Reductions, B. and S. Numbers	Ready-to-finish Gauge, In.
4	4, 6, 6, 6, 6	0.0317
8	6, 6, 6	0.050
12	4, 4, 6	0.0795
14	6, 6	0.100
16	4, 6	0.1245
18	4, 4	0.159
20	6	0.200
22	4	0.2525
24	Milled to .317	0.317
26		0.399

That all this material, which received low reductions and high anneals in processing, should be essentially random in orientation prior to the final reduction is indicated by the fact, reported by Palmer and Smith,[1] that such material will not produce ears. This observation was confirmed, as reported in a later section (see Fig. 9*b*).

The progressive perfection of the (110)-[112] deformation texture with increasing reductions was observed by single photograms on all specimens of the series. The deformation textures following reductions of 8, 20 and 34 B. and S. numbers are shown in Fig. 2.

One-hour anneals at 400°C. were given to specimens that had been given all the indicated reductions. Complete pole figures

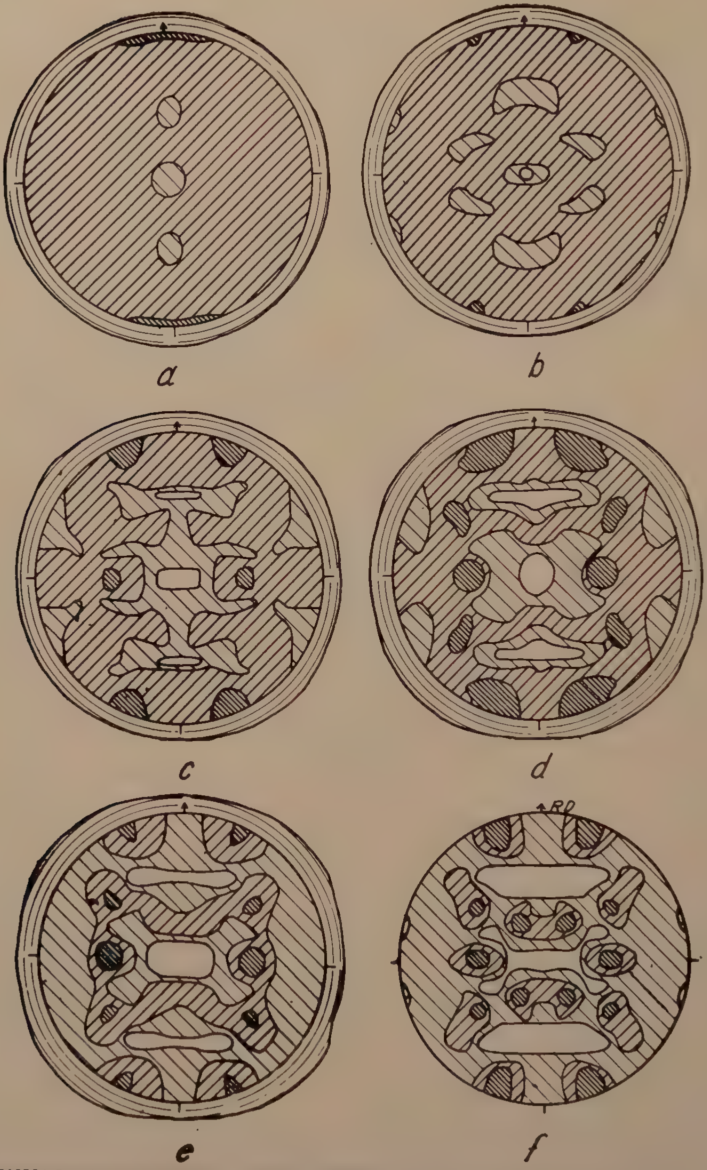

FIG. 3.—CHANGES IN RECRYSTALLIZATION TEXTURES AND EARING BEHAVIOR WITH INCREASING REDUCTIONS.

70-30 Brass annealed 1 hour at 400°C. following reductions of B. and S. numbers: (*a*) 12; (*b*) 16; (*c*) 20; (*d*) 24; (*e*) 26; (*f*) 34. (Octahedral pole figures, rolling direction vertical.)

were made on those which had been rolled 12, 16, 20, 24 and 26 B. and S. numbers, and these are reproduced in Fig. 3*a* to *e*. The contours of the cups drawn from these materials are indicated with these pole figures. The progressive perfection of the so-called (113)[112] texture with increasing deformation is accompanied at reductions of 20 B. and S. numbers and more by a gradual development of ears at 45° from the rolling direction. The texture obtained from material rolled 34 B. and S. numbers to 0.0063 in. is included (Fig. 3*f*) to show the complete perfection of the texture. It might be noted here that, at least for fine-grained material, the departure from random structure can be more readily detected with X-rays than by cupping the material.

Remarkably different from the recrystallization textures at low temperatures were those found when the material from this rolling series was annealed at 700°C. for one hour. The reported variations in ear position become clearer in the light of this series. Pole figures were plotted for specimens that had been given reductions of 12, 14, 16, 20, 24 and 26 B. and S. numbers, and these, with the cup contours, are reproduced in Fig. 4. All of these textures seem to involve various distributions around (110)[112]. The texture for 700°C. following 12 B. and S. numbers reduction (Fig. 4*a*) has a fourfold symmetry; with increasing reductions there is a gradual change to a threefold symmetry having six peripheral concentrations of octahedral poles. The transition textures show a rather complete spread of octahedral poles around the whole periphery. For the greatest reduction, the regions of primary intensity have developed in the positions surrounding peripheral octahedral poles for the ideal (110)[112] texture.

The ear positions follow the texture. For 12 B. and S. numbers reduction, the fourfold symmetry of the texture corresponds with four ears at about 50° from the rolling direction. During the transition to the threefold symmetry, the ear height lessens and the same four ears shift closer to the transverse direction. At 20 B. and S. numbers reduction the cup shows the six-ear form. In fact, this pole figure is very similar to that published by Burghoff and Bohlen[2] for material that produced six ears. At higher reductions, the four ears near the transverse direction increase considerably in height so that the contour becomes one of four ears at about 55° from the rolling direction separated by deep troughs in the transverse direction.

Two strips of 65-35 brass that had been given special production schedules in the mill were available for examination. One of these had been given a special balanced reduction schedule described by Palmer and Smith (1) as a schedule that will produce low ears in spite of high reductions. This material was rolled 13 B. and S. numbers, annealed to a grain size of 0.120 to 0.200 mm. and finally rolled 15 B. and S. numbers. The texture and cup contour of this material following a 700°C. anneal are given in Fig. 5*a*. Comparison with Fig. 4 will show that the texture and low ear height fit very well in this series between 14 and 16 B. and S. numbers. The low ear height is very probably due to the uniform peripheral distribution of (111) poles. The other mill-produced strip was given a final reduction of 18 B. and S. numbers, following a series of low reductions and high anneals, with the intention of producing material that would give six ears. Again the pole figure and cup contour, shown in Fig. 5*b*, are very consistent with the series illustrated in Fig. 4.

Changes with Temperature of Final Anneal

It is apparent from the foregoing results that the temperature of final anneal has a conspicuous effect on the recrystallization

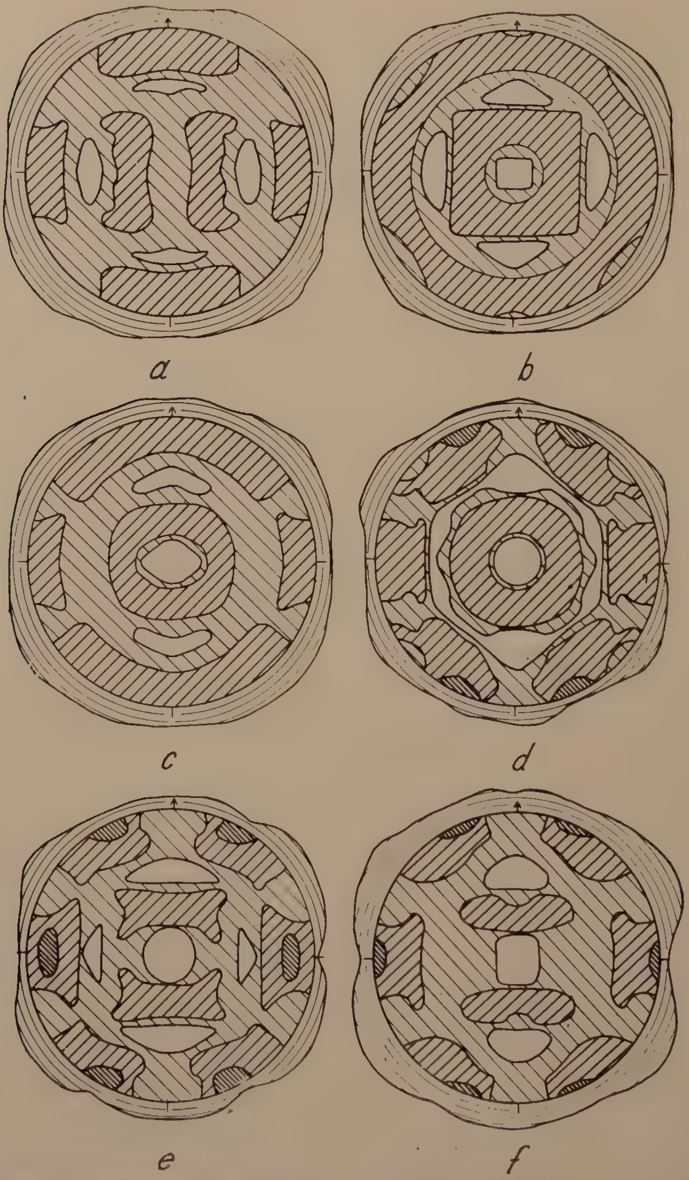

FIG. 4.—CHANGES IN ANNEALING TEXTURES AND EARING BEHAVIOR WITH INCREASING REDUCTIONS. 70-30 brass annealed 1 hour at 700°C. following reductions of B. and S. numbers: (*a*) 12; (*b*) 14; (*c*) 16; (*d*) 20; (*e*) 24; (*f*) 26. (Octahedral pole figures, rolling direction vertical.)

or "annealing"* texture, and it would be interesting to know more specifically how this texture changes with temperature. A series of pole figures (Fig. 6) was made from material rolled 34 B. and S. numbers (to a gauge that would not permit the drawing of satisfactory cups) and annealed at 400°, 500° and 600°C. for one hour. With increasing temperature, some of the central octahedral poles disappear and new concentrations form in the transverse directions. Near the center of the pole figure. the (111) poles tend to concentrate around their ideal positions for the (110)[112] texture. The pole figure, Fig. 6d, was obtained from material rolled 30 B. and S. numbers and annealed at 650°C. This texture constitutes an almost perfect (110)[112] orientation and its indicated perfection is greater than that of any other pole figure obtained in this research.†

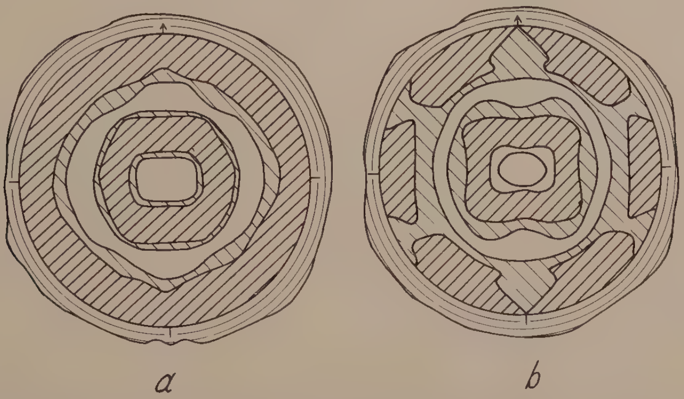

FIG. 5.—ANNEALING TEXTURES AND EARING BEHAVIOR OF MILL-PRODUCED 65-35 BRASS, ANNEALED 1 HOUR AT 700°C.

(*a*) Rolled 13 B. and S. numbers, high anneal, rolled 15 B. and S. numbers. (*b*) Rolled 18 B. and S. numbers following low reduction, high anneal schedule.

(Octahedral pole figures, rolling direction vertical.)

The development of the (110)[112] texture by high-temperature anneals is again confirmed in the pole figure shown in Fig. 6*e*. This texture was obtained from material annealed at 750°C., rolled 26 B. and S. numbers (95 per cent) to 0.020 in. and annealed for one hour at 750°C. Although the reduction is considerably less, the same high-temperature annealing texture is obtained.

The difference between textures after low and high temperatures of anneal raises the question as to whether there is a different type of nucleation when the hard strip is placed in a furnace at a high temperature. Is the (110)[112] annealing texture characteristic of a higher temperature of nucleation or does it result from a change in over-all texture accompanying grain growth? No tests were made on very rapidly heated specimens, but the possibility of texture changes with grain growth was confirmed.

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* The textural difference between a low-temperature anneal, resulting in recrystallization to a fine grain, and a higher temperature anneal, resulting in recrystallization and grain growth, is so great that our terminology might well be altered to conform to these results. It is proposed here that "recrystallization" texture be employed for the very fine grained material and "annealing" texture for material heated well into the grain growth range.

† The probable reason for this may be that the photograms from which this pole figure was plotted were among the earliest made from large grained material, and the average intensities were weaker than those obtained later with improved techniques. The result would be that regions of primary intensity would be narrowed and more easily separated from regions of lesser intensity. This would give the pole figure an appearance of higher concentration around the ideal positions.

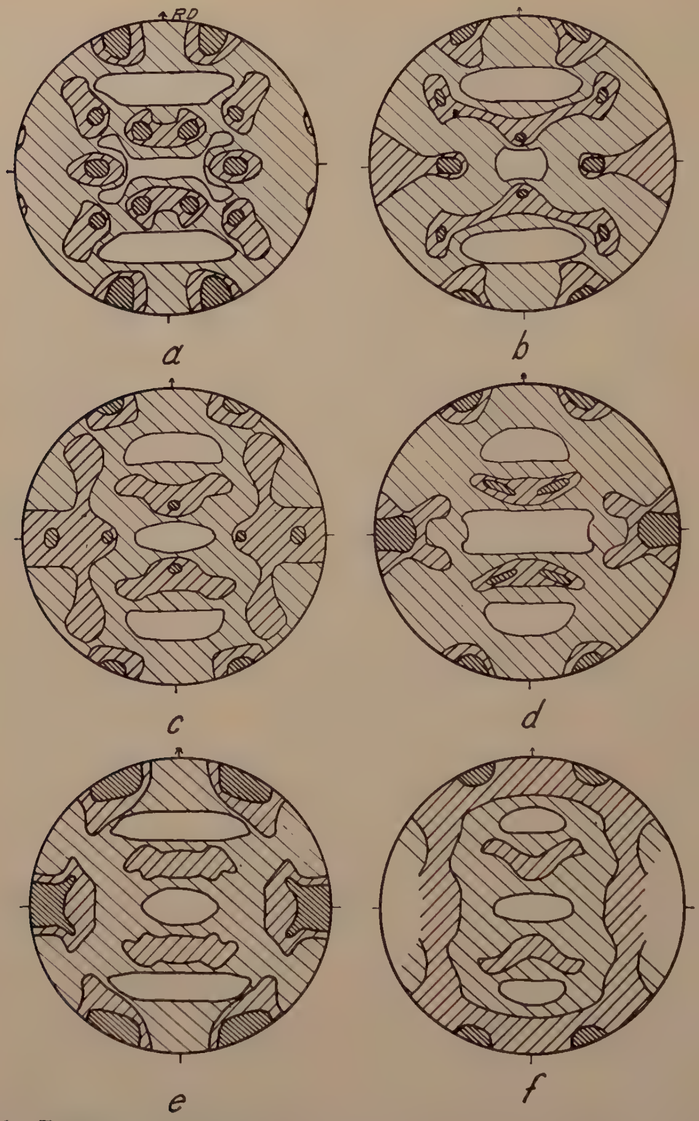

Fig. 6.—Effect of temperature of final anneal on texture of 70-30 brass

a. Rolled 34 B. and S. numbers, annealed 1 hour at 400°C.
b. Rolled 34 B. and S. numbers, annealed 1 hour at 500°C.
c. Rolled 34 B. and S. numbers, annealed 1 hour at 600°C.
d. Rolled 30 B. and S. numbers, annealed 1 hour at 650°C.
e. Rolled 26 B. and S. numbers, annealed 1 hour at 750°C.
f. Severely rolled and annealed from one end with gas flame.
(Octahedral pole figures with rolling direction vertical.)

Brass rolled 34 B. and S. numbers was annealed for 24 hr at 250°C. It was found that this material was completely recrystallized and had the same texture as material annealed at 400°C., i.e., nominally (113)[112]. The specimen was then replaced in a furnace at 700°C. for one hour, and upon examination was found to have developed the characteristic (110)[112] high-temperature texture.

The mechanism of change in texture with increasing temperature of final anneal is difficult to understand. It is inconceivable that any one grain can change its orientation under thermal stress alone. Therefore, it seems probable that a comparatively few grains existing in a (110)[112] orientation at low temperatures are much more stable thermally than the other grains and that these grow with increasing temperature at the expense of the other grains.

In an attempt to learn why a grain of a specific orientation should be more stable than another, it was noted that grains with (110) planes parallel to the sheet surface have more octahedral planes lying perpendicular to the surface of the sheet than grains otherwise oriented. Since the direction of the thermal gradient developed when sheet specimens are placed in the furnace is usually in a direction normal to the sheet surface, it was thought possible that this relationship between the positions of the octahedral planes and the direction of thermal gradient might have some bearing on the selective grain growth.

In order to check this hypothesis, specimens were annealed from one edge. This was done by immersing the specimen in a crucible full of finely powdered Sil-O-Cel with one edge projecting through an asbestos cover. A gas flame was applied at this edge resulting in thermal flow through the specimen to the far edge. A pole figure was obtained from a specimen so annealed that was hot enough to have recrystallized completely throughout its whole length. This specimen had parallel bands of crystals representing different temperatures of anneal. Because of the design of the camera it could only be photographed with one direction vertical, thereby complete coverage of the projection was prevented. The pole figure, shown in Fig. 6*f*, was obtained as completely as possible from the smaller grained end of this specimen where the grain size was about 0.075 mm. The direction of heat flow was the same as the rolling direction and since the region subsequently examined was about 2 in. from the gas flame, the thermal gradient must have been through the specimen in the rolling direction. The texture is very close to that obtained by normal annealing processes at 600°C. (Fig. 6*c*), at which temperature a grain size of about 0.065 mm. was developed. Differences can be noted, but it is certain that the preferred orientation in the end-annealed specimen is best rationalized as (110)[112]. Consequently, it is unlikely that the direction of thermal gradient influences selective grain growth.

Inasmuch as satisfactory cups could not be drawn from the 0.0063-in. material, another series was run to measure the effect of final annealing temperature on texture and earing behavior. The maximum reduction obtainable was 26 B. and S. numbers (95 per cent). Specimens from this strip were annealed for one hour at 400°, 500°, 600°, 700° and 750°C. The pole figures and cup contours obtained from these specimens are shown in Fig. 7. The same general observations of changing texture can be made of this series as were made in the previous section. The texture at 500°C. (Fig. 7*b*) looks more like a combination of the initial and final textures than a stage in a continuous progressive shift in orientations; i.e., it is not probable that at intermediate temperatures there are appreciable numbers of grains having intermediate orientations. Traces of the low-temperature texture have disappeared at 700°C. (Fig. 7*d*). If comparison is made with Fig. 6, it

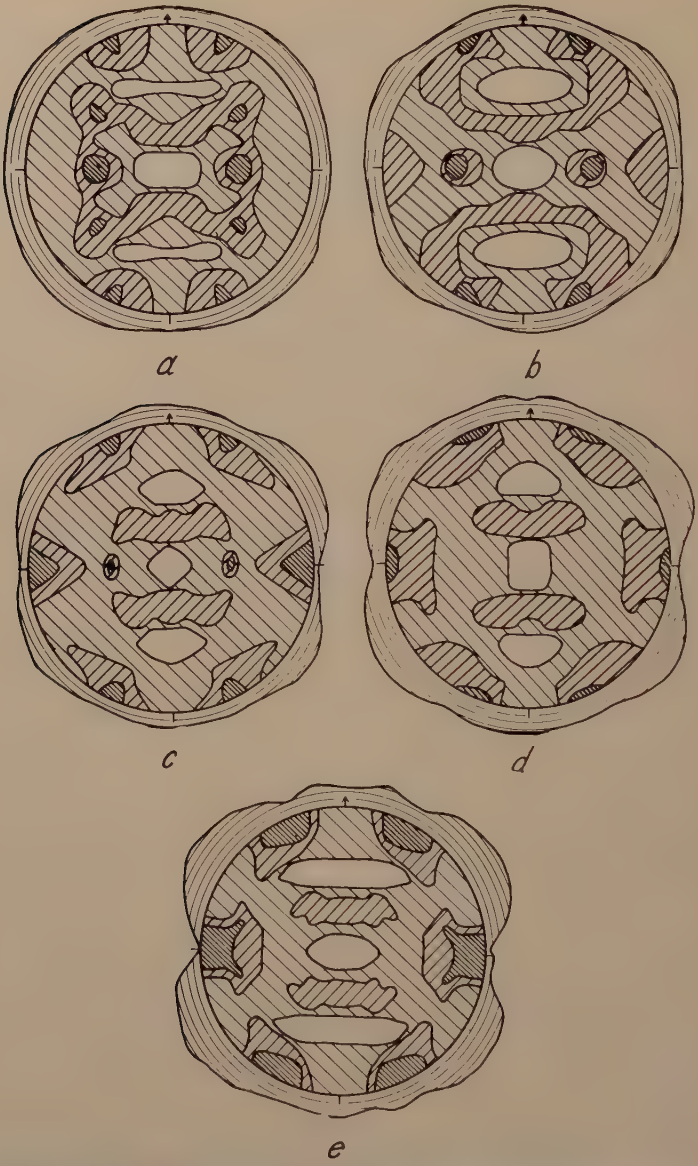

Fig. 7.—Changes in texture and earing behavior with temperature of final anneal. 70-30 brass rolled 26 B. and S. numbers and annealed 1 hour at: (*a*) 400°C.; (*b*) 500°C.; (*c*) 600°C.; (*d*) 700°C.; (*e*) 750°C.

(Octahedral pole figures, rolling direction vertical.)

will be seen that for final anneals of 500° and 600°C. more of the low-temperature texture remains if the reduction is 34 B. and S. numbers than if it is 26 B. and S. numbers.

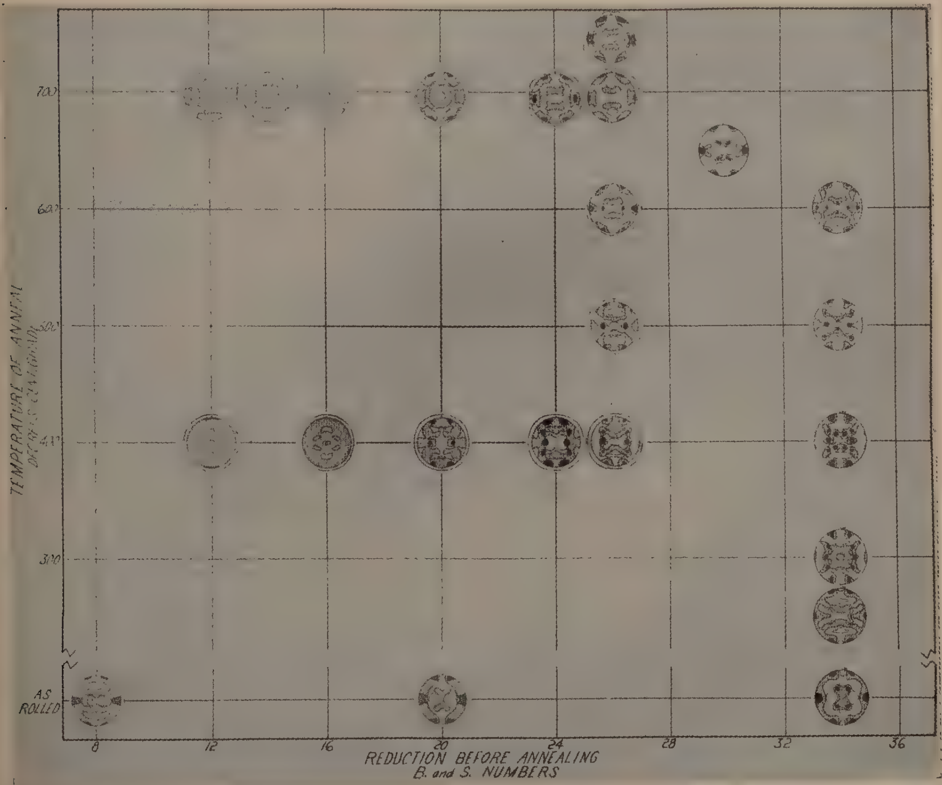

FIG. 8.—CHANGES IN TEXTURE AND CUP CONTOUR OF 70-30 BRASS WITH AMOUNT OF REDUCTION AND TEMPERATURE OF FINAL 1-HOUR ANNEAL.
(Octahedral pole figures, rolling direction vertical.)

For the purpose of providing better visualization of how texture and earing behavior are related to amount of reduction and temperature of anneal, the accumulated pole figures with their associated cup contours have been assembled into a single chart, as shown in Fig. 8. Pole figures for 70-30 brass rolled 34 B. and S. numbers and partially recrystallized in one hour at 250° and 300°C. are included in addition to those already presented.

A general survey of the pole figures for annealed brass reveals three characteristically located vacant areas, indicating absent orientations, which are common to both recrystallization and "annealing" textures. These vacant areas occur along the diameter in the rolling direction. Moreover, the orientations indicated by these areas are the ones that first disappear from the recrystallization texture as the amount of deformation is increased (Fig. 3*a*).

Accompanying the change in texture with temperature is a shift in ear direction from 45° to about 55° from the rolling direction. The cup contour found at the high temperatures shows an occurrence of troughs at the peripheral (111) pole concentrations. The presence of ears at peripheral (111) voids is not so well defined.* appreciably to the tendency to form higher ears. Without quantitative support, however, it is felt that the more important

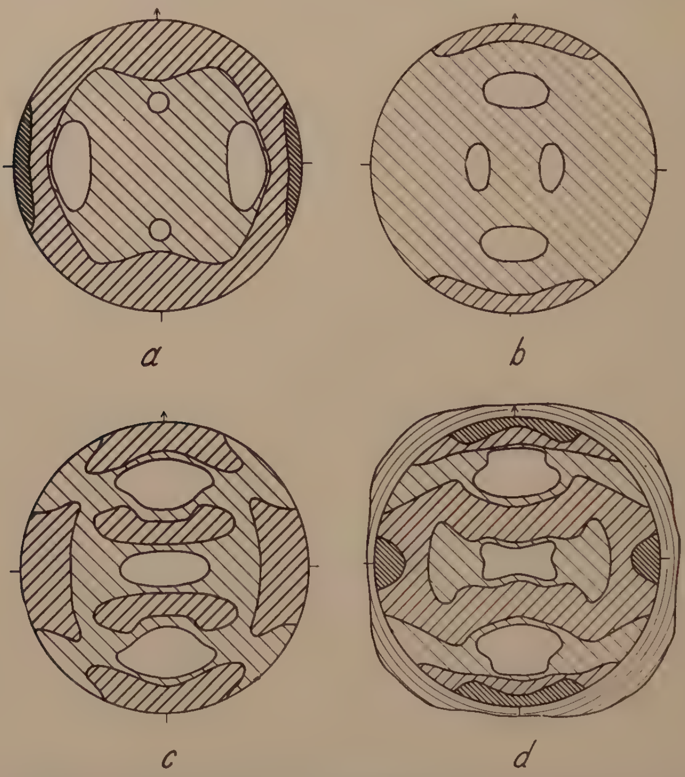

FIG. 9.—TEXTURES FROM PRODUCTION SCHEDULES INVOLVING SMALL REDUCTIONS.
70-30 brass rolled 4 to 6 B. and S. numbers between anneals.
a. Running-down anneals of 1 hour at 400°C., texture at final reduction.
b. Final anneal at 400°C. of material *a* and final anneal at 650°C. of material with running down anneals of 1 hour at 650°C.
c. Final anneal at 650°C. of material *a*.
d. Mill schedule—low reductions, low anneals, final anneal at 700°C.
(Octahedral pole figures, rolling direction vertical.)

influence is the increased grain size, which permits greater ease of plastic flow.

The question raised earlier, concerning the increase in ear height with temperature of final anneal, has two contributing answers. It seems doubtful that the perfection of the (110)[112] texture is any greater than that of the (113)[112]. The presence of more peripheral (111) pole concentrations in the former may add

Development of Directionality with Low Reductions

Palmer and Smith[1] have reported that brass produced by a series of low reductions, 6 B. and S. numbers, will develop nonearing structures if the processing anneals are 650°C. or higher; if the anneals are around 400°C. a final high anneal will produce a structure that gives very high ears at 45°. The preferred orientations accompanying such schedules were investigated. Pieces of the same 0.400-in. cartridge brass were given five consecutive reductions by rolling of about 6 B. and S. numbers each to a gauge of 0.014 in. They were finished from this gauge by a reduction of 4 B. and S. numbers to 0.009 in. One of the pieces, called "random," received anneals of one hour at 650°C. at each step; the other piece, called "preferred," received anneals of one hour at 400°C.

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* The absence of well-developed ears in the rolling direction (a peripheral void) for a texture such as in Fig. 7*e* may have some connection with the absent orientations responsible for the vacant areas.

The deformation texture of the "preferred" material is illustrated in Fig. 9*a*. It seems to differ from the deformation texture, obtained by rolling 8 B. and S. numbers from essentially random material (Fig. 2*a*), chiefly in a lack of concentrations of octahedral poles away from the periphery of the pole figure.

X-ray examination of the "random" specimen given a final anneal at 400°C. showed a barely detectable variation in intensity around Debye rings. When annealed at 650°C., the variations in intensity were still very slight, but a pole figure of the distribution was attempted. A texture that was practically identical with this was obtained from the "preferred" material that was given a final anneal of 400°C. These textures are illustrated by the single pole figure, Fig. 9*b*. It will be seen that practically no preferred orientation developed.

A final anneal of 650°C. on the "preferred" material gave a definite texture. It showed a general scatter about a (110)[112] texture, including poles in the rolling direction. This texture is illustrated in Fig. 9*c*. It is remarkably similar to Fig. 4*a* for material rolled 12 B. and S. numbers and annealed at 700°C. and to the pole figure published by Burghoff and Bohlen for material producing four ears.[2]

Some material was available that had been given a similar production schedule in the mill to that used in producing the "preferred" specimen. The pole figure showing the texture of this material as annealed at 700°C. is illustrated in Fig. 9*d*. A distinct similarity can be noted between this and Fig. 9*c*. Since this mill-produced material had a gauge of 0.020 in., satisfactory cups could be drawn from it. The contour is plotted around the pole figure and shows the characteristic high four 45° cups which Palmer and Smith[1] have shown to be produced by such a schedule.*

Effect of Rolling (110)[112] *Texture*

It was felt that the results of this research might have some bearing on the interpretation of the differing effects of high and low *intermediate* anneals as discussed in the previous section. Without investigation of the effect of rolling fine-grained material, the whole interpretation cannot be known. However, high annealing temperatures, even following comparatively low reductions, have been found to produce a texture that can be defined as a scatter around (110)[112]. The textural effect of rolling material having this preferred orientation and subsequently recrystallizing it was next investigated.

Baldwin[10] has shown that copper having a "cubic" texture will have this texture broken up by rolling and that subsequent annealing will result in recrystallization into a new texture. It would be interesting to know how brass behaves under similar treatment.

Material that had been rolled 30 B. and S. numbers and annealed at 650°C., producing the texture shown in Fig. 6*d* and again in Fig. 10*a*, was rolled in its original rolling direction 12½ B. and S. numbers. The resultant deformation texture is given in Fig. 10*b*. The octahedral poles tend to spread in the rolling direction, particularly those in the transverse peripheral positions. When this material was recrystallized at

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* On the basis of the evidence in this section, it is probable that the texture, directionality and ears which Cook and Richards[7] found in annealed fine-grained brass after rolling 10 to 50 per cent was present in the brass before rolling.

400°C. and at 700°C. the textures were very weak (Fig. 10*c* and *d*).

It seems certain that the use of high intermediate anneals tends toward a random final orientation with low earing tendency because rolling and recrystallization break up preferred orientations that are developed by high-temperature anneals.

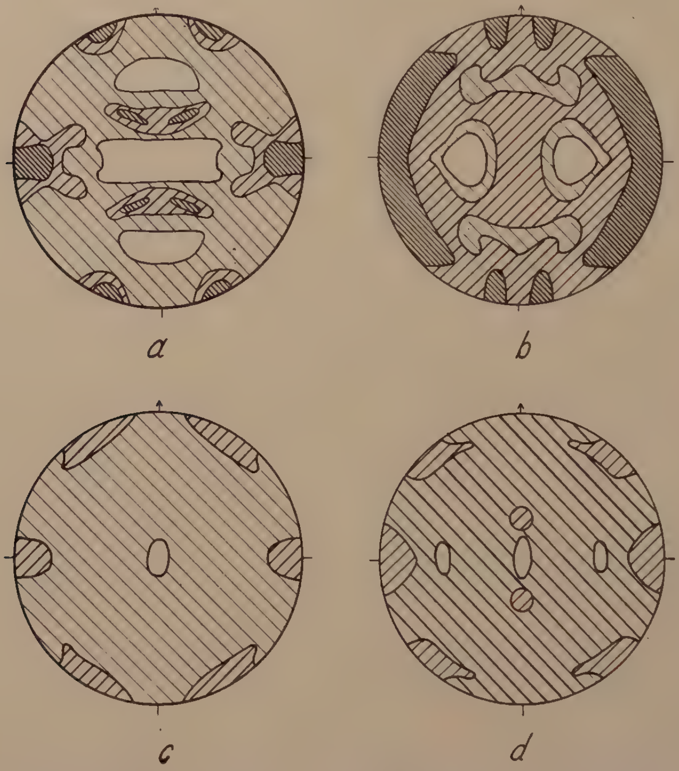

FIG. 10.—EFFECT OF ROLLING 70-30 BRASS HAVING (110)[112] TEXTURE.

a. (110)[112] texture from rolling 30 B. and S. numbers and annealing at 650°C.
b. Material *a* rolled 12½ B. and S. numbers in same direction.
c. Material *b* annealed 1 hour at 400°C.
d. Material *b* annealed 1 hour at 700°C.
(Octahedral pole figures, rolling direction vertical.)

The Recrystallization Process

The common conception of the recrystallization process includes the formation of nuclei of new grains and the simultaneous existence of recrystallized and deformed grains in partially recrystallized metal. Excellent micrographs showing the latter condition in brass were given by Maddigan and Blank.[11] In severely rolled brass, the deformed grains have a well-developed texture and so do grains that form by complete recrystallization at 400°C. Moreover, it has been shown that texture can be altered by temperature of anneal. The question that obviously arises is: Is the orientation of the recrystallized grains that first form in severely rolled brass nearer to the deformation texture than to the texture at 400°C.?

Specimens of 70-30 brass were rolled 34 B. and S. numbers and annealed for one hour at 100°, 150°, 200°, 250°, 300° and 350°C. Photograms were made using a glancing X-ray beam on specimens rotated 64° about the rolling direction as an axis from the position normal to the beam. These are shown in Fig. 11. It will be observed that in this portion of the Debye rings, there are no spots in the (002) ring for the deformed material. Spots appear in this ring at 250°. These spots are in the same orientation at 250° as they are at 350° and, when comparison is made with other photograms, this is also the position of spots for the 400°C. anneal.

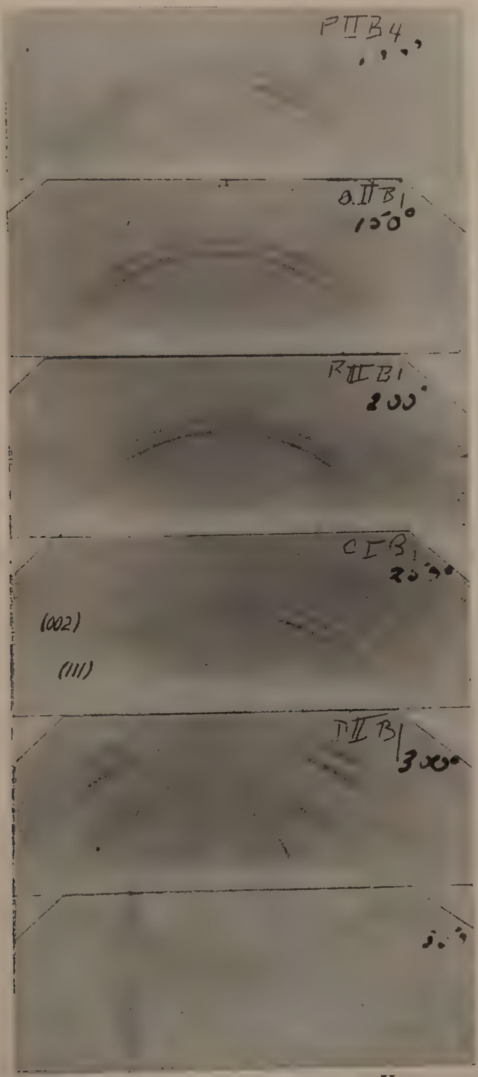

FIG. 11.—RECRYSTALLIZATION AS DISCLOSED BY X-RAY DIFFRACTION.
Glancing photograms from unetched stationary specimens of brass rolled 34 B. and S. numbers and annealed 1 hour at indicated temperatures.

When transmission photograms are taken with specimens rotated 21° about the rolling direction as an axis, the patterns obtained for the deformation texture and the 400°C. recrystallization texture are markedly different. This specimen position therefore is suitable for the examination of partially recrystallized material. Photograms obtained in this position for the deformation texture, for a specimen annealed one hour at 250°C., and for a specimen annealed one hour at 400°C., are shown in Fig. 12. The pattern obtained for the material annealed at 250°C. consists of a combination of the other two patterns. It should be particularly noted that for the deformation texture there are no orientations that will produce spots on the right side of the (111) ring at 90° to the vertical (rolling) direction, but at 400°C. there is a sharp concentration at this position. Again, intensities present along the right side of the (002) ring for the deformation texture are absent for the 400°C. texture. It can then be seen that the material at 250°C. contains both of these groups of spots and that the recrystallized material present lies in the orientation of the recrystallization texture.

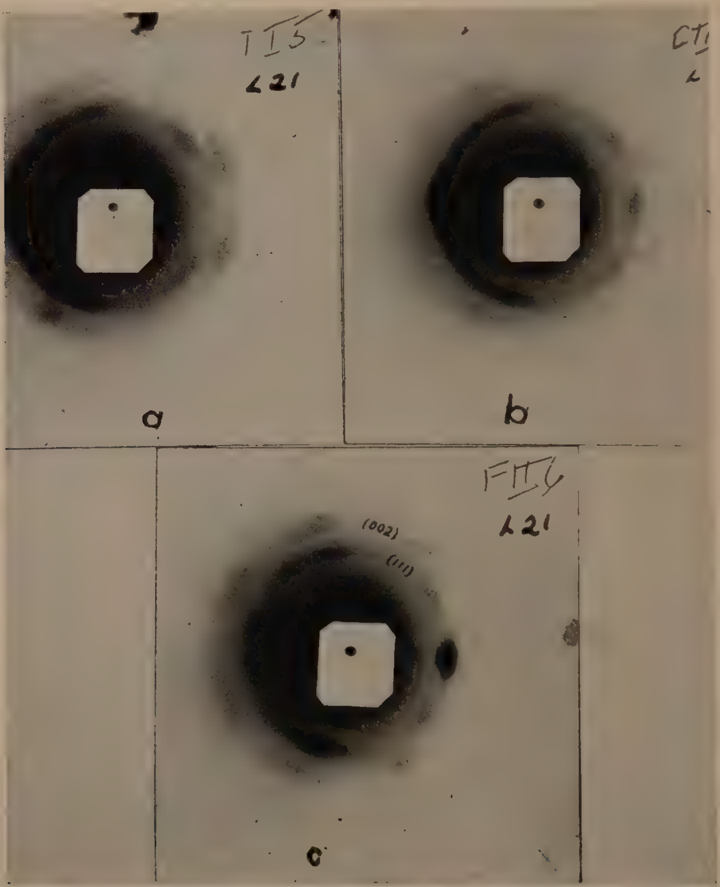

Fig. 12.—Appearance of grains in (113)[112] orientation at 250°C.
Photograms taken at same specimen position for (*a*) brass rolled 34 B. and S. numbers; (*b*) same brass annealed 1 hour at 250°C.; (*c*) same brass fully recrystallized in 1 hour at 400°C.

This direct X-ray evidence that the first detectable recrystallized grains have the same orientation as the completely recrystallized material can be integrated by means of pole figures. It has been pointed out that, after a one-hour anneal at 250°C., severely rolled brass is just beginning to recrystallize. A pole figure for a specimen so annealed is shown in Fig. 13*a*. Alongside this pole figure is a composite of the secondary intensities* of the deformation and 400° recrystallization textures (see Figs. 2*c* and 3*f*). There is a strong similarity between the composite and the 250° texture, indicating that severely rolled brass, when partially recrystallized, consists of deformed crystallites clustered about one orientation, (110)[112], and new grains clustered around another, (113)[112].

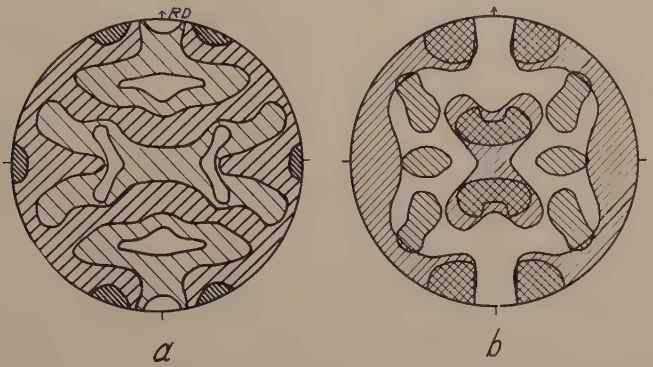

FIG. 13.—TEXTURE OF PARTIALLY RECRYSTALLIZED 70-30 BRASS COMPARED WITH COLD-ROLLED AND FULLY RECRYSTALLIZED TEXTURES.

(*a*) Rolled 34 B. and S. numbers, annealed 1 hour at 250°C.

(*b*) Composite of secondary intensities of deformation texture and 400°C. recrystallized texture.

(Rolling direction vertical.)

The failure of this evidence to relate the orientation of recrystallized grains directly to an orientation of the deformation texture, is partially compensated for by the deductive evidence that grains having the deformation texture, (110)[112], must be present in barely recrystallized material since they would be the only source of this orientation in its development at high temperatures.

The results of this research give a fairly complete picture of the orientations accompanying the recrystallization and grain growth of severely rolled brass. As a result of deformation, the crystallites have orientations distributed around (110)[112] in common with other face-centered cubic metals. When heated to the point where recrystallization has developed new grains of sufficient magnitude and number to be detected by X-ray diffraction, these grains are found to cluster around an orientation usually described as (113)[112]. Upon complete recrystallization there must exist a combination of two orientations, (113)[112] and (110)[112], in such unbalanced proportions that grains having the latter orientation make no detectable contribution to the over-all texture. As the temperature of anneal is increased, the grains having a (110)[112] orientation prove to be more stable and grow at the expense of the other grains. The proportions of the orientations are steadily altered until at 650° to 700°C. grains in the (113)[112] orientation make no detectable contribution to the over-all structure.

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* Inclusion of primary intensity regions, which would have enhanced the comparison, was sacrificed to avoid confusion of overlapping concentrations.

MECHANISM OF EAR FORMATION

In general, investigators of the problem of earing have been content to study the anisotropy of the strip, and investigators of texture have not been directly concerned with the problem of earing. Correlation of anisotropy and earing behavior is inadequate unless it is shown how it contributes to the ear formation during the drawing of a cup. Moreover, the failure of such correlations to account for the difference between brass and copper may result from failure to consider some fundamental factor, for example, the influence exerted by their different textures. Since both earing behavior and anisotropy of mechanical properties are functions of slip plane orientation, it should be profitable to analyze them in terms of preferred orientation.

There has been general agreement that in brass, ears occur in directions of minimum tensile strength and maximum elongation.[2,7] Palmer and Smith[1] have shown that the modulus of elasticity in brass, which produces four ears, is at a minimum in the direction of ears.

Copper and other face-centered cubic metals that recrystallize to the (100)[001] texture have a minimum elongation at 0° and 90° to the rolling direction, and these are the directions in which ears form. Like brass, the modulus of elasticity for copper having this texture is at a minimum in the direction in which ears form.

As for a correlation between directionality of mechanical properties and texture, there have been very few observations in the literature. Referring to a pole figure for brass that produces four ears, Brick (discussion in ref. 2) has pointed out that the maximum elongation at 45° to the rolling direction might be expected from the positions of concentration of octahedral poles. In this direction the octahedral planes are most favorably oriented for slip to take place. Aside from the efforts of Cook and Richards,[8] previously referred to, there seem to have been no other attempts to interpret earing behavior in terms of both anisotropy and texture.

Review of the cup contours for the rather widely variable textures herein reported leads to some suggestions for correlation between earing behavior and texture. Neglecting the low-temperature textures, it was noted that troughs occurred rather consistently in the directions of peripheral octahedral pole concentrations and that ears, less conspicuously, occurred away from these concentrations. Ear formation is related to stresses in the plane of the sheet during the cupping operation, and these stresses develop different resolved shear stresses on slip planes according to direction. Stresses in the plane of the sheet that lie in directions away from peripheral octahedral pole concentrations would be expected to develop greater resolved shear stresses on the corresponding octahedral planes than those in the directions of the concentrations. Thus slip would be easier under stresses in the former directions, and these are the ear directions.

It is probable that the chief reason for failure to achieve satisfactory interpretations of the mechanism of ear formation in terms of preferred orientation and anisotropy lies in the complexity of stresses and the nonuniform pattern of plastic flow, which are present when directional material is drawn into a cup. In its simplest form the stress pattern can be considered to consist of: (1) Circumferential compressive stresses involved in reducing the diameter of the blank; (2) radial tensile stresses from the action of the punch; and (3) almost negligible normal compressive stresses. Swift[12] has shown by theoretical calculations that at the outer edges of the blank the circumferential compressive stresses predominate, and that near the shoulder of the die the radial tensile stresses are much greater. Interpretation of the mechanism of ear formation must include consideration of the compressive stresses.

The low twofold symmetry of the (110)[112] texture found in brass suggested that measurements of directionality on this material would be revealing. Moreover, there was a possibility that determinations of directionality in rate of work-hardening, a property that had not previously been taken into account, might not encounter the contradictions found when earing behavior is considered in relation to other mechanical properties in copper and brass. Finally, failure to include directionality of properties in compression has been due to lack of suitable equipment for measuring compressive properties on sheet metal. Fairly satisfactory results can be obtained in measuring these properties by the use of equipment which has recently been developed.[13]

Anisotropy in Annealed Copper and Brass

Brass having the (110)[112] orientation, and copper having the (100)[001] orientation, were tested in tension and compression, the data including rates of work-hardening. Specimens of 0.020-in. gauge having a texture of (110)[112] were obtained by rolling 0.400-in. gauge 70-30 brass, annealed at 700°C., 26 B. and S. numbers (95 per cent) and annealing at 750°C. The strip so obtained was about 3 in. wide. A 3-in. wide strip of copper having the "cubic texture" was obtained by annealing hard copper one hour at 400°C. at 0.503-in. gauge and rolling it to 0.035 in. (23 B. and S. numbers, or 93 per cent) and annealing at 500°C. The "cubic" orientation expected from this schedule was confirmed micrographically. All specimens were annealed after machining. Most of the tests in tension and compression were carried out using Huggenberger extensometers. These tests were stress-strain tests covering the elastic and plastic regions up to 0.9 per cent total strain in compression and tension and, for brass, to fracture in tension. The brass specimens in the tensile-elastic range were tested by dead-weight loading, measuring strain with Tuckerman extensometers. The precision for these tests was considerably greater than for those employing Huggenberger extensometers, and it was possible to determine the 0.0001 per cent offset.

When the data for both compressive and tensile stress-strain tests were plotted, it was found that in the plastic range the points could be made to fit two consecutive straight lines of slightly different slope. Although straight lines would hardly be expected to be the true stress-strain curve, this fortuitous observation made it possible to assign numerical values to rate of work-hardening. The slope (rate of work-hardening) in the early part of the curve is recorded as "A" and in the second part as "B." To illustrate the feasibility of using such arbitrary measures of rate of work-hardening, typical stress-strain curves in compression are presented in Fig. 14.

True stress-true strain curves were plotted from the tensile data from 2 per cent total strain to fracture in the case of brass. For this range the data followed straight lines, but since these were true stress-true strain curves, the slopes were of a different order of magnitude from other rate of work-hardening values and only relative variations with direction can be compared.

For the brass, specimens were taken at 0°, 18°, 36°, 54°, 60°, 72° and 90° from the rolling direction. Except for the 60° specimen, these directions are close to positions around the periphery of the (110)[112] pole figure of poles of planes having low indices. Since the texture of copper had a high order of symmetry characteristic of the "cubic" texture, specimens were taken at 0°, 22½° and 45° to the rolling direction.

Values for the measured mechanical properties of the brass are plotted against direction in Figs. 15 and 16. These are

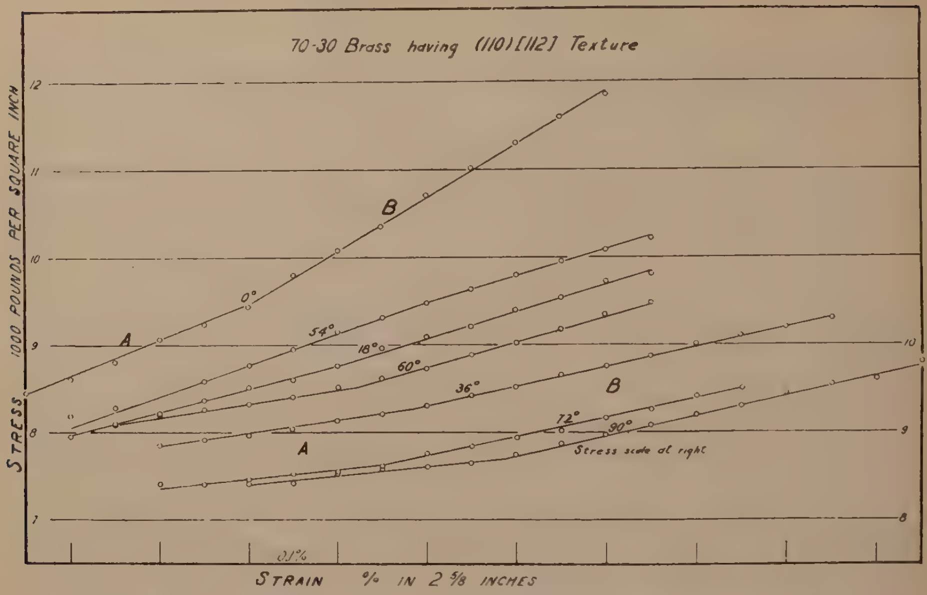

FIG. 14.—TYPICAL CURVES FOR RATE OF WORK-HARDENING EVALUATION.
Points fall close to two consecutive straight lines. (Angle of specimen from rolling direction indicated. Scale at right for 72° and 90° specimens.)

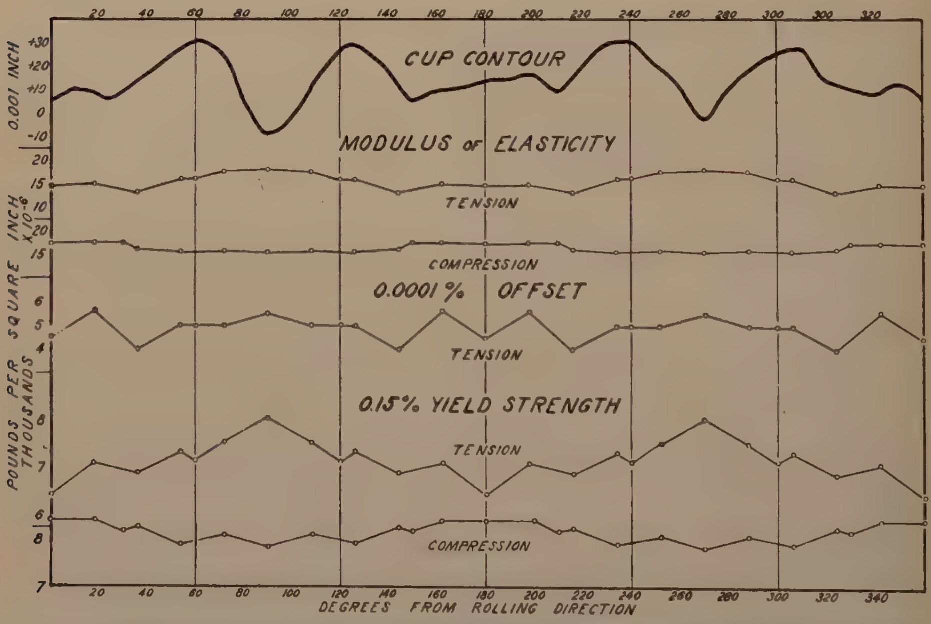

FIG. 15.—DIRECTIONAL VARIATIONS IN SOME MECHANICAL PROPERTIES OF BRASS HAVING (110)[112] TEXTURE AS COMPARED WITH CONTOUR OF CUP FROM SAME MATERIAL.
70-30 brass annealed 700°C., rolled 95 per cent, annealed 750°C.

plotted with reference to the actual cup contour of a cup drawn from the same material. Tensile values are plotted at the angle of the specimen. However, since compressive stresses in the cupping blank are at right angles to the radial direction, the properties in compression for material in the blank that lies along a radius in the rolling direction should be those that were measured on a specimen at 90° to the rolling direction. This is true of any position around the blank; consequently, the values obtained from the stress-strain curves in compression are plotted at 90° from the specimen direction.

It will be observed that the modulus of elasticity in tension exhibits a slight maximum at the position of the major trough of the cup contour, a relationship that is consistent with that found in four-eared cups. However, the minimum modulus of elasticity occurs nearer another trough than an ear. There seems to be little correlation between the properties shown in Fig. 15 and the cup contour. However, rates of work-hardening in tension and compression do vary consistently with cup contour (Fig. 16). Although the rates of work-hardening in the A and B parts of the stress-strain curves in tension show rather minor variations with direction, as compared with the rates of work-hardening in compression, the variations of both are consistent in direction with cup contour. Maximum rates of work-hardening in both tension and compression lie in that part of the blank which is at 90° from the rolling direction or at points where the major troughs of the cup contour form. Lesser peaks in these curves are found at about 35° from the rolling direction and are close to the positions of minor troughs, 30°. Minima in the work-hardening curve for both tension and compression

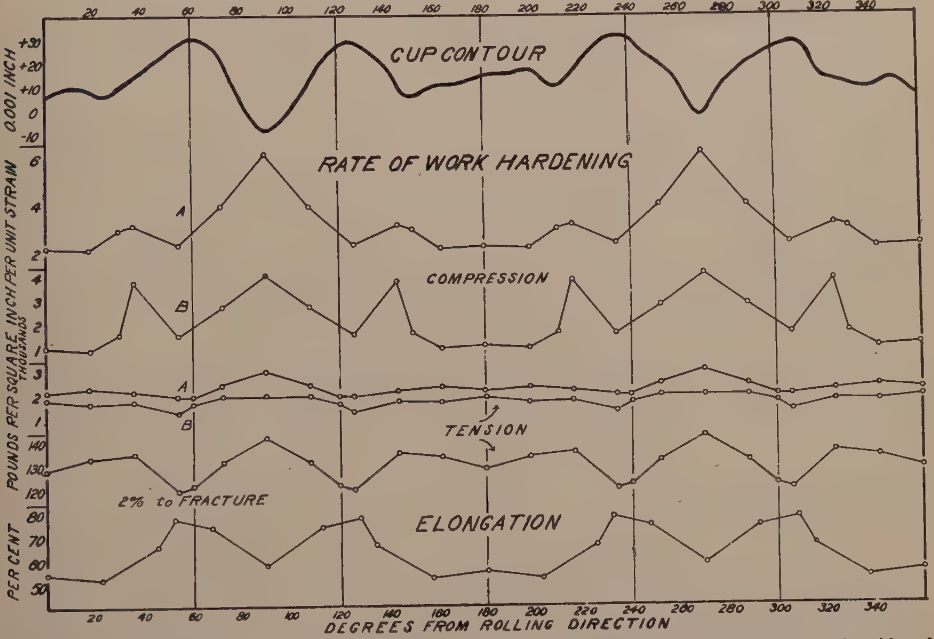

FIG. 16.—DIRECTIONAL VARIATIONS IN SOME MECHANICAL PROPERTIES OF BRASS HAVING (110)[112] TEXTURE AS COMPARED WITH CONTOUR OF CUP FROM SAME MATERIAL.
70-30 brass annealed 700°C., rolled 95 per cent, annealed 750°C.
(Elongation data from Phillips and Samans.[2])

occur at 54° to 60° from the rolling direction or at the positions of the major ears. In and around the rolling direction the rates of work hardening in tension are average to high, while in compression they are low. In this region, where these effects counteract each other somewhat, cup contour is rather flat.

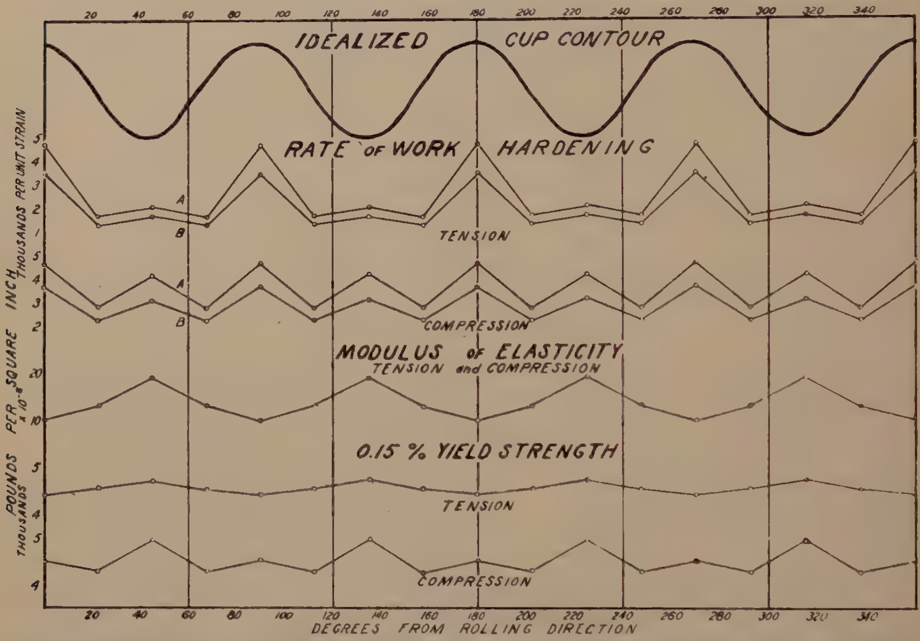

FIG. 17.—DIRECTIONAL VARIATIONS IN SOME MECHANICAL PROPERTIES OF COPPER HAVING "CUBIC" TEXTURE AS COMPARED WITH IDEAL CUP FORM.
Copper annealed at 400°C., rolled 93 per cent, annealed at 500°C.

Remembering that in the curves of work-hardening in compression the values are offset 90° from the actual specimen direction, it will be seen that specimens in the same direction (for tension and compression) will show considerable differences in rate of work-hardening. In spite of these differences, the properties in tension and compression combine, in different azimuthal positions around the blank, to form a consistent pattern of high and low rates of work-hardening.

The results of the tests on "cubic" copper at 0°, 22½° and 45° to the rolling direction are plotted against direction in comparison with an idealized cup contour in Fig. 17. The cup contour follows the variations in modulus of elasticity more closely than variations in rate of work-hardening. Moreover, in direct contradiction to the deductions made in the case of brass, the ears occur in the directions of maximum rate of work-hardening in both tension and compression. It is evident, therefore, that the same dissimilarity exists in this case between copper and brass as has been observed when cup contour is related to elongation.

In spite of the consistency between copper and brass that is found when the directionalities of their moduli of elasticity are compared, it does not seem probable that these differences should have any effect once plastic flow has started. Assuming constant strain around the blank, the positions of high modulus would yield first and tend to equalize the stresses. Once plastic flow has started, differences in elastic modulus should have little effect.

Earing Behavior and Texture

Failure to find any simple relationship between the direction at which ears form and directional mechanical properties, which will apply to both the copper and brass textures, leads one to seek an interpretation based on their different crystallographic orientations. In the first section, it was concluded that for a number of different textures, the ear position corresponded in direction with low peripheral concentrations of (111) poles and the troughs with high peripheral concentrations. Since there are no peripheral (111) poles in the "cubic" texture of copper, comparison is difficult.

Oversimplified explanations from a crystallographic approach, such as those of Cook and Richards,[8] can be very misleading. Without making claim to a complete crystallographic explanation, comparison of the brass and copper textures suggests what may possibly be a significant condition. There is one conspicuous similarity between the two materials when their earing behavior is related to their textures. In both cases, ears occur in the directions where circumferential compressive forces act in a [100] direction. For copper, material in the blank at 0° and 90° to the rolling direction, i.e., the ear direction, is under radial tensile forces acting normal to one set of cube planes and circumferential compressive forces acting normal to another set. This is the crystallographic direction in which maximum resolved shear stresses are developed on all four sets of slip planes. The major applied stress near the perimeter of the blank is the circumferential compressive stress. The supplementary presence of radial tensile stresses would promote slip on (111) planes in a [110] direction which would be parallel to the plane of the sheet on all sets of slip planes.

In the complementary (110)[112] texture for brass, there is a (110) pole at about 54° from the rolling direction. Circumferential compressive forces acting in the portion of the blank at 54° from the rolling direction would be acting in a [100] direction. In this case the radial tensile forces, acting in a [110] direction, promote slip along all four sets of slip planes at 30° to the plane of the sheet.

As an aid in visualizing this relationship, a schematic representation of the crystal structures of the copper and brass in their preferred orientation with respect to the cupping blank is presented in Fig. 18. Octahedra, bounded by the (111) planes of a unit cube, are used as models. The octahedron for brass is placed at 54° from the rolling direction and the one for copper is at 90°, both being in the direction of ear formation.

The perspective is based on a view of the models from a point just above the near edge of the blank on a line with its center. Half of each octahedron lies above, and half below the plane of the blank. The blank itself is somewhat out of perspective, giving the impression that it is being viewed from a much higher point than that from which the models are viewed.

Tensile stresses in radial directions and compressive stresses in a circumferential direction are indicated by large arrows. It is apparent that the compressive stresses act in a [100] direction for both textures. For copper, the radial tensile stress, in another cube direction, directs the slip along the plane of the blank in the directions indicated by the small arrows. For brass, as indicated by the small arrows, the slip would be in a direction at 30° to the plane of the blank, whether radial tensile stresses are present or not.

Here, then, we have combined compressive and tensile forces acting, in the metal forming the ear, to promote radial flow of crystals so oriented that the compressive stresses develop maximum resolved shear stresses on all sets of octahedral planes in both brass and copper. In the trough direction for copper, the compressive forces act on only two sets of slip planes, while the tensile forces act on the other two. In the trough direction for brass, the tensile forces act in a [111] direction, a position of minimum resolved shear stress on the slip planes.

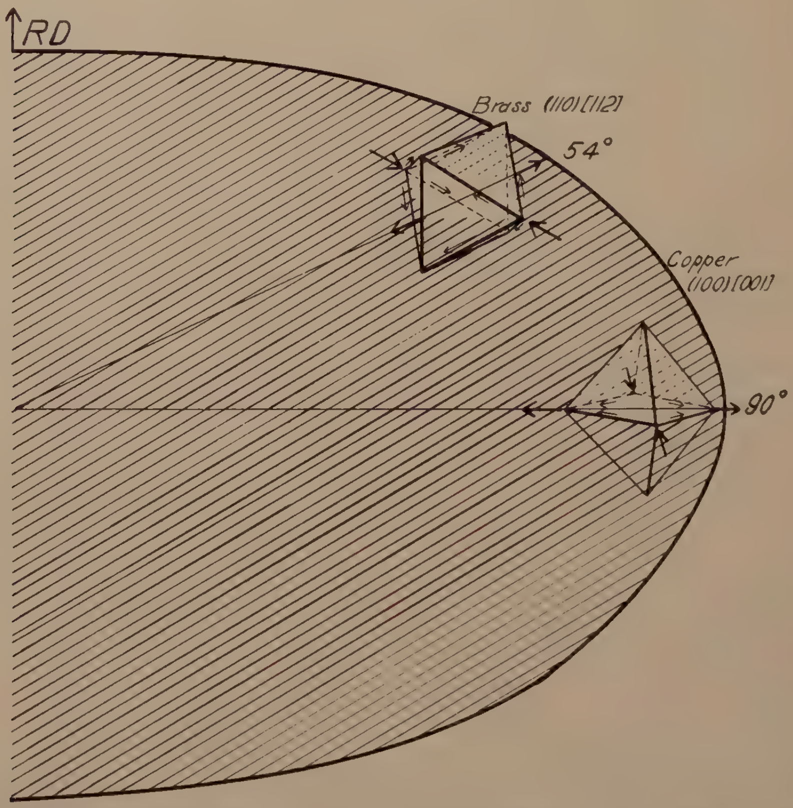

Fig. 18.—Orientations of annealed brass and copper shown diagrammatically in cupping blank.

Large arrows show direction of major stresses; small arrows indicate slip direction.

Previous mention has been made of the conviction that the mechanism of ear formation is far more complex than the simple relationships herein emphasized would imply. The principal reason for this conviction is the probability that development of ears is influenced by orientation clear up to the time when the last of the blank is drawn over the shoulder of the die, and that orientation and flow patterns change with deformation and with the changing shape of the flange throughout the process. The simplified analysis refers to the early part of the draw. However, the shape of the flange of partially drawn cups generally varies only quantitatively throughout the draw, ears appearing at the beginning of the draw in approximately their final positions.

Summary

1. The first detectable new crystals formed upon annealing severely rolled

brass sheet with a (110)[112] deformation texture, have the well-known (113)[112] low-temperature (400°C.) recrystallization texture.

2. Annealing at a high temperature (600° to 700°C.) results in establishment of the (110)[112] texture even when a preliminary anneal gives the (113)[112]. Apparently, undetectable new grains in the (110)[112] orientation grow at the expense of grains having other less stable positions.

3. Increasing degrees of deformation prior to a 400°C. anneal result only in progressive perfection of the (113)[112] *recrystallization* texture. Increasing deformations followed by 700°C. anneals gives a variety of distributions around the (110)[112] *annealing* texture. These variations account for four and six-ear cup contours.

4. A (110)[112] texture, developed in brass by a high reduction and high penultimate anneal is almost entirely destroyed by rolling 12 B. and S. numbers and annealing, even at high temperatures.

5. Low reductions and low intermediate anneals with a final high anneal produce material that gives high ears at 45° and a corresponding texture of fourfold symmetry, inadequately described as (110)[112].

6. Study of a variety of textures and corresponding cup contours reveals an approximate correlation: troughs lie in the direction of high peripheral concentrations of (111) poles, ears in the direction of low peripheral concentrations.

7. Compression and tension tests of brass having a (110)[112] texture and copper having a (100)[001] texture showed that a correlation between rate of work-hardening in both tension and compression and earing behavior could be made for the brass but not for the copper.

8. From a crystallographic approach, it was found that for both brass and copper, ears occur in that azimuthal position on the cupping blank in which the crystals are so oriented that cirumferential compressive stresses act in the direction which develops maximum resolved shear stresses on the four sets of octahedral (slip) planes: i.e., the [100] direction. Radial tensile stresses direct the flow in the plane of the blank for copper and at 30° to this plane for brass.

ACKNOWLEDGMENT

The authors wish to express sincere appreciation to Mr. John R. Freeman, Jr., Technical Manager of The American Brass Co., for invaluable cooperation in furthering this research, in particular by affording to one of the authors (F. H. W.) the opportunity to carry out a much more extensive investigation than otherwise would have been possible.

Many stimulating discussions with Mr. E. W. Palmer during its inception and development are gratefully acknowledged.

The authors wish, too, to express their thanks to Mr. G. Nelson, of the Hammond Laboratory, for construction of the camera and his valuable suggestions pertaining thereto.

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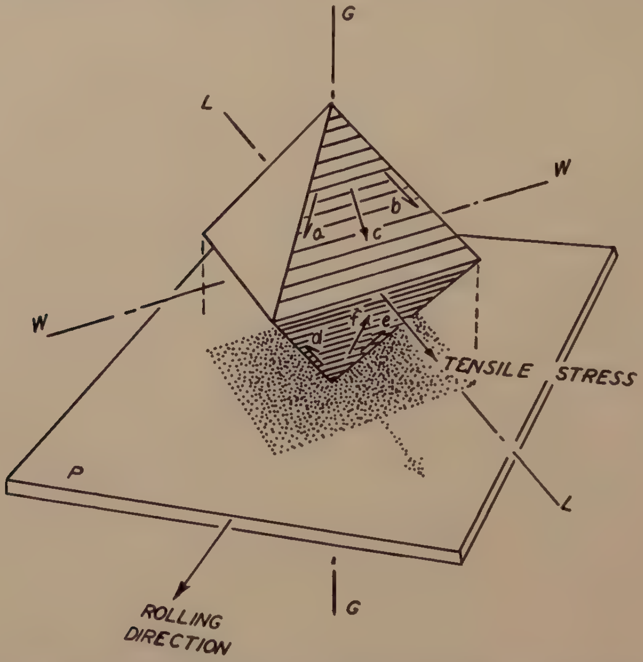

FIG. 19.—COPPER STRIP.

Rolling plane labeled *P* and rolling direction indicated by arrow. Superimposed upon the strip is the slip octahedron in its appropriate cubically aligned orientation. For a tensile test taken at 45° to the rolling direction, the stress is as indicated by the arrow. Slip occurs on the two shaded planes in the directions *a* and *b*, and *d* and *e*. Since the slip on each plane occurs in these directions simultaneously and equally, these directions may be supplanted by *c* and *f*, respectively.

DISCUSSION

W. M. BALDWIN, Jr.[*]—This writer has read Dr. Wilson and Dr. Brick's very comprehensive paper on the earing tendencies of brass. His only comment is made with reference to the suggested mechanism of earing for copper and brass described in the section headed "Earing Behavior and Texture" and graphically depicted in their Fig. 18. In this section the authors say, "Previous mention has been made of the conviction that the mechanism of ear formation is far more complex than the simple relationships herein emphasized would imply. The principal reason for this conviction is the probability that development of ears is influenced by orientation clear up to the time when the last of the blank is drawn over the shoulder of the die, and that orientation and flow patterns change with deformation and with the changing shape of the flange throughout the process." The writer agrees with this belief and, further, wishes to suggest another factor that makes the process more complex: the contaminating effect of the two complementary (110) [1$\bar{1}$2] orientations on each other in the case of brass. While he has no direct evidence of this effect in cupping, the writer does have some evidence of it in the case of relative deformation rates involved in a tensile test on highly oriented copper and brass.

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[*] Chase Brass and Copper Co., Cleveland, Ohio.

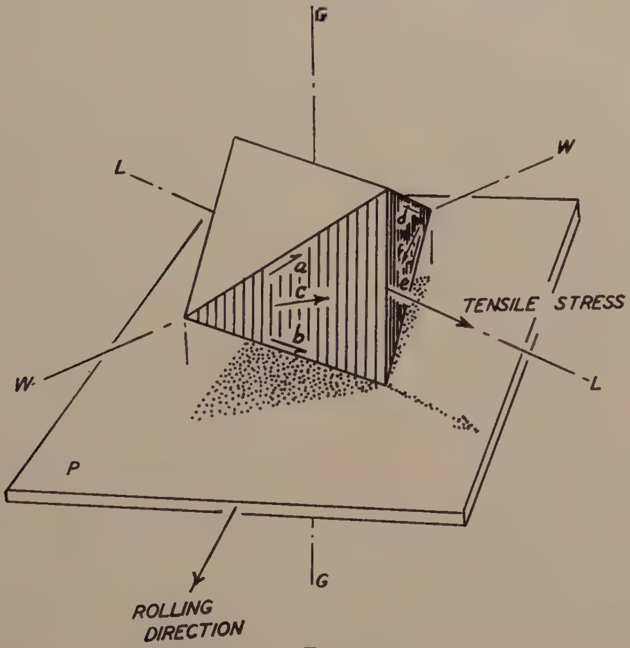

FIG. 20.—BRASS STRIP.

Rolling plane labeled P and rolling direction indicated by arrow. Superimposed upon the strip is one slip octahedron corresponding to one half of the complementary (110) [1$\bar{1}$2] orientation. For a tensile test taken at 54° to the rolling direction, the stress will be as indicated by the arrow. In this case, by analogy from the case of copper strip, slip will occur on the shaded planes in the directions a and b, and d and e. Since slip occurs on each plane equally and simultaneously along these two sets of directions, they may be supplanted by the directions c and f, respectively.

In a recent paper,[14] it has been shown, on the basis of X-ray data and the deformations involved, that when cubically aligned soft copper strip is pulled in tension at 45° to the rolling direction, slip occurs on the two octahedral planes and in the two [211] directions indicated in the accompanying Fig. 19. With this slip system there is a diminution of the gauge dimension GG almost equal to the elongation encountered in the length dimension LL. There is a negligible change in the width dimension WW.

In Fig. 20, the case for brass is treated. If only one half of the (110) [1$\bar{1}$2] complementary orientation is treated, it would appear that a tensile test taken at 54° to the rolling direction would cause slip to occur on the two octahedral planes and in the two [211] directions indicated in illustration. In this case it would follow that there would be a diminution of the width dimension WW almost equal to the elongation encountered in length dimension LL. Little change in the gauge dimension (GG) would be expected. Tensile tests conducted on (110) [1$\bar{1}$2] brass in our Cleveland Laboratory do not, however, confirm these presumptions.

It appears then that simple prognostication of the deformation behavior in a tensile test of cubically aligned copper and of (110) [112] brass is impossible on the basis of a comparative study of the slip octahedra of one half of the complementary (110) [1$\bar{1}$2] orientation in brass and of the (001) [100] orientation in copper. Perhaps many factors prevent such a comparative study; certainly it would be expected that the other half of the complementary (110) [1$\bar{1}$2] orientation in brass would be one such factor.

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[14] Baldwin, Howald, and Ross: A.I.M.E. *Tech. Pub.* 1808 (1945).

Whether any of the above considerations are involved in the cupping process, the writer is in no position at the present time to say.

F. H. Wilson and R. M. Brick (authors' reply).—It appears to the authors that it would be quite acceptable to reason by analogy that, even as simple interpretations of behavior in tensile testing cannot be achieved on the basis of slip octahedra of half of a complementary texture, the same limitation interferes with a similarity simplified analysis of the mechanism of ear formation. We are grateful for Mr. Baldwin's emphasis on this point and for his excellent diagrams, which also contribute considerably to the clarity of the paper's discussion of slip octahedra.

Phantom Laminations in Brass

By Daniel R. Hull,* Member A.I.M.E., H. F. Silliman,† and John R. Freeman, Jr.,‡ Member A.I.M.E.

(New York Meeting, February 1945)

In the normal operation of a brass-rolling mill, sheet and strip has, for the most part, been finished in comparatively thin gauges, involving a substantial amount of cold-work and a considerable number of anneals. This condition has been disturbed by the preponderance of cartridge brass, which is not rolled to thin gauges, and particularly by brass for artillery cartridge cases, on which the mill may finish its work at a thickness between 0.400 and 0.900 in. Obviously, the amount of rolling and the number of anneals to which such a product can be subjected are small compared with strip that is carried to a thickness of a few hundredths of an inch. As a result, critical examination into the internal condition of metal has been made on an extensive scale at a stage of manufacture that would not, in normal times, have been chosen for complete inspection.

Under these conditions, a type of defect has been recognized that is not seen at thinner gauges. It might be more accurate to call it the appearance of a defect, since it refers to an apparently laminated, discontinuous structure, which, in fact, does not exist as such, and disappears after suitable treatment. For this reason it has been called a phantom lamination, which the authors consider an appropriate term. It is the purpose of this paper to describe the phenomenon and the conditions of its occurrence and, at least tentatively, to discuss its nature and cause.

Great numbers of phantoms may be found in 2:1 brass, either hot-rolled or cold-rolled. They are also found in 70-30 brass, sometimes when hot-rolled and generally when cold-rolled. It is not believed that phantoms are confined to these alloys but this paper is limited to them for the purpose of description.

Hot-rolled 2:1 Brass

For illustration, therefore, a typical cake of hot-rolled 2:1 brass has been chosen. This was rolled to a slab 7/8 in. thick, from a casting 5 in. thick by 24 in. wide by 18 in. high, which was believed to have been sound. After hot-rolling and cooling, the slab was sheared and a portion of such a shear cut is shown in Fig. 1. It would be difficult to convince anyone viewing this specimen that the metal was not unsound. The impression would be confirmed by the appearance of a tensile break, as shown in Fig. 2. This is an ordinary tensile-test piece from metal just described. Although there was nothing in its tensile strength or elongation that suggested unsoundness, it appeared run through with pipes and laminations. To question the reality of such a condition would imply questioning the obvious. But, considering the history of the metal, it would be difficult to believe that it could be so bad as it appeared. It seemed reasonable, though, that if the defects were what they appeared to be, they could be traced back from the sheared or broken face.

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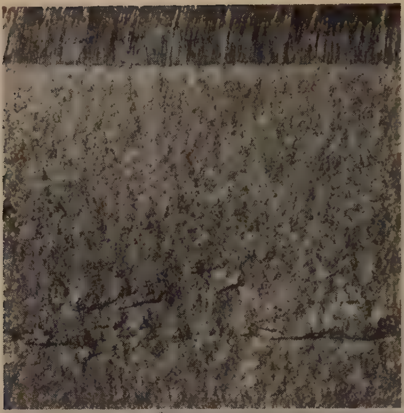

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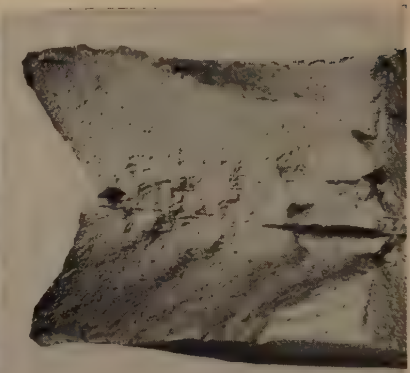

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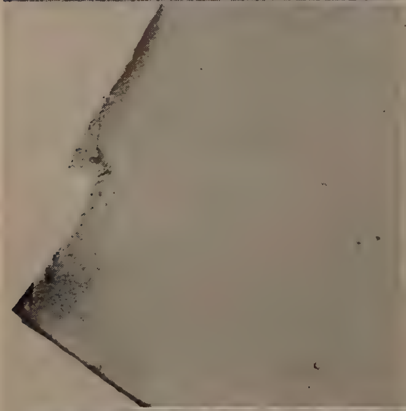

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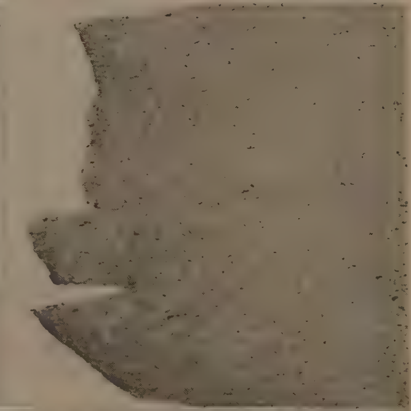

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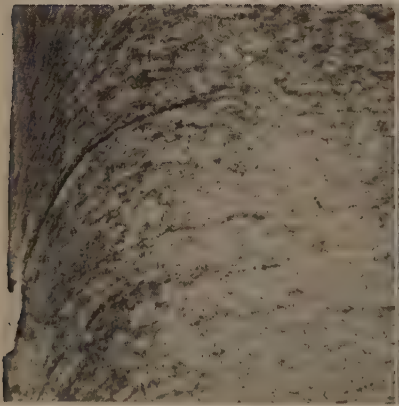

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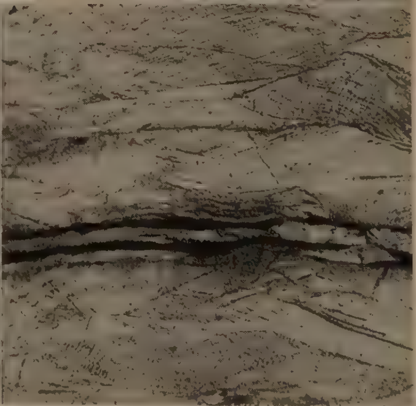

Fig. 1.—Shear cut, 2:1 brass as hot-rolled. × 2.5.
Fig. 2.—Tensile fracture, 2:1 brass as hot-rolled. × 4.
Fig. 3.—Lengthwise section through shear cut shown in Fig. 1. × 3.
Fig. 4.—Lengthwise section through tensile fracture shown in Fig. 2. × 7.
Fig. 5.—Lengthwise section through shear cut of hot-rolled 2:1 brass showing phantom associated with beta phase. × 37.5.
Fig. 6.—Detail of beta string shown in Fig. 5. × 300.

Figs. 3 and 4 represent an attempt to do this. Some of the worst areas in the metal represented in Figs. 1 and 2 were sawed through at 90° to the shear cut and the sawed surface was prepared for the microscope. Fig. 3 is a profile of Fig. 1; Fig. 4 a profile of Fig. 2. The main body of the metal is entirely sound, and the laminations do not extend appreciably back from the face of the shear cut, but the ragged contours of the profile account for the apparent laminations.

Fig. 5 shows further details of a profiled shear cut. It is from the same metal as that shown in Figs. 1 and 3. The dark line beginning at the notch and curving upward is beta. In shearing, the metal has been torn for a short distance along this line. Phantoms frequently are associated with beta and frequently end in a beta string. This feature of the general subject will be discussed later.

Fig. 6 shows a detail of the beta and the surrounding metal, all of which is sound so far as is revealed at 300 diameters.

Phantoms such as those shown are typical of any slab of hot-rolled 2:1 brass. If such metal is held for a substantial time at an elevated temperature, they may be modified, but it is difficult to remove them entirely by heat-treatment.

For instance, Fig. 7 shows a profile of a shear cut from the same metal shown in Figs. 1, 3, 5, 6 and 8, which, after hot-rolling, has been heated for one hour at 600°C. and then sheared. The beta, to all intents and purposes, has been absorbed, but the nature of the shear cut has been only sightly modified.

Fig. 8 shows the face of a shear cut of the same piece of metal, held for 24 hr. at 600°C. after hot-rolling. The laminated appearance is still not quite gone.

If a simple heating of the specimen has a modifying effect on phantoms, it might be inferred that such effect is due to diffusion, and, if so, the effect would be accelerated by cold-rolling and annealing. This proved to be true. In fact, all trace of phantoms disappeared when the hot-rolled metal shown in Fig. 7 was given a substantial anneal, cold-rolled and annealed again, thus:

Hot-roll 5 to ⅞ in.
Anneal 1 hr. at 700°C.
Roll to 0.600 in.
Anneal 30 min. at 575°C.

The shear cut was then smooth and compact as shown in Fig. 9.

It is not attempted to say what the minimum requirement in annealing and rolling may be. In some instances an hour at 600° has been sufficient, in place of the above 700°; in other instances the intermediate anneal at 600° has been insufficient. That probably depends on previous conditions. But it can be shown that, unless the anneal at some point is adequate—that is, unless it is sufficiently hot and prolonged—phantoms may persist through a number of rolling and annealing cycles. For example: A portion of the bar shown in Fig. 1 (⅞ in. thick, hot-rolled) was overhauled to ⅝ in. and rolled in three successive stages of about 30 per cent each, and annealed at each stage, thus:

Roll	Anneal Briefly
⅞ in. to 0.430..........	575°C.
0.430 in. to 0.287.......	575°C.
0.287 in. to 0.200.......	575°C.

At each anneal the metal was held in the furnace only until it attained temperature, and immediately taken out. The conventional aspects of annealing, such as recrystallization and grain growth, had been satisfied, but the effect on the appearance of the shear cut was hardly appreciable. Except that the laminations appeared narrower, it looked just as bad at 0.200 in. as at ⅞ in. (Fig. 10). The point to be emphasized is that, at some stage there must be at least one process anneal (i.e., not the final anneal) of sufficiently sustained temperature and duration. It is believed that this particular requirement is based on the necessity for diffusion.

COLD-ROLLED 70-30 BRASS

The appearance of phantom laminations in cold-rolled brass is similar to that already described.

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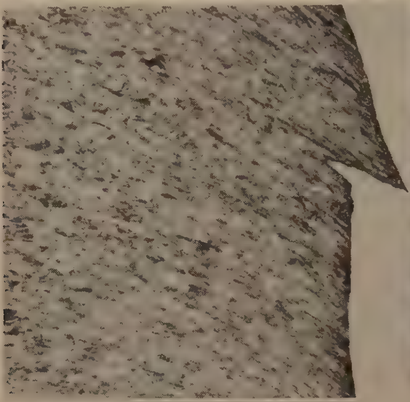

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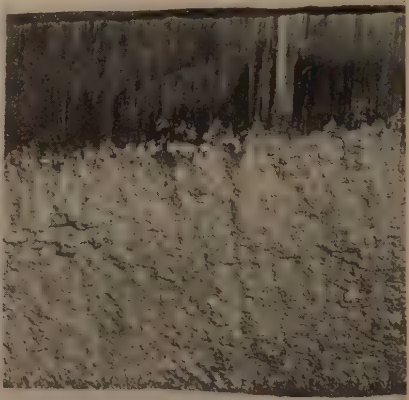

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FIG. 7.—LENGTHWISE SECTION THROUGH SHEAR CUT IN HOT-ROLLED 2:1 BRASS ANNEALED TO ABSORB BETA PHASE. CF. FIG. 5. × 37.5.

FIG. 8.—SHEAR CUT 2:1 BRASS, HOT-ROLLED AND ANNEALED 24 HOURS AT 600°C. × 2.5.

FIG. 9.—SHEAR CUT 2:1 BRASS, HOT-ROLLED, ANNEALED 1 HOUR AT 700°C., REDUCED 30 PER CENT BY COLD-ROLLING AND ANNEALED 30 MINUTES AT 575°C. × 4.

FIG. 10.—SHEAR CUT 2:1 BRASS, HOT-ROLLED THEN ALTERNATELY COLD-ROLLED WITH 30 PER CENT REDUCTION AND ANNEALED BRIEFLY AT 575°C. THROUGH THREE CYCLES. × 3.5.

For purposes of illustration, 70-30 brass has conveniently been chosen. All the examples here cited were cast in a slab $2\frac{1}{16}$ in. thick by $19\frac{1}{2}$ in. wide by 56 in. long, from a water-cooled mold of the Junker type.

Phantoms may be found in the early stages of cold-work, but disappear in a cycle of adequate annealing and cold-rolling. Yet they may persist through a number of such cycles in the absence of an adequate anneal. These are the characteristics already described, but because the cold breakdown is a very different process from hot-rolling, a few observations with respect to cold-rolled metal are offered.

Fig. 11 shows phantoms in cold-rolled 70-30 brass. It was cast as mentioned above, $2\frac{1}{16}$ in. thick, cold-rolled to 1.040 in. and briefly annealed at 600°C. The lines in the cross section have the appearance of discontinuities and considerable care is necessary to determine whether or not they represent actual cavities.

Fig. 12 shows another example of phantoms in 70-30 brass, one stage further along in mill work. Its mill-treatment history was as follows:

Cold-roll 2$\frac{1}{16}$ to 1.040 in.
Anneal ½ hr. at 450°C.
Cold-roll 1.040 to 0.620 in.
Anneal ½ hr. at 450°C.

The anneals purposely were held to a minimum.

It has the appearance of being infested with flattened-out pipes and laminations. This appearance is also present in the tensile break shown in Fig. 13. The mill-treatment history of this specimen was similar to the preceding, i.e.:

Roll 2$\frac{1}{16}$ to 1.040 in.
Anneal ½ hr. at 450°C.
Roll 1.040 to 0.620 in.
Anneal ½ hr. at 625°C.

Although the appearance of the broken sample is very bad, the metal contains no voids, as shown in Fig. 14, which is a longitudinal section through Fig. 13. It shows the ragged nature of the fracture, which accounts for its laminated appearance. This is seen to better advantage in Figs. 15 and 16. The deep notches on one side are really matched by corresponding protuberances on the other, although this correspondence is not shown in the photomicrographs. There is a shattered condition for several hundredths of an inch behind the break, which is consistent with the selective nature of the fracture and obviously is a part of it. There is nothing in the tensile strength or elongation suggestive of inferiority.

The effect of annealing temperature is further shown in Fig. 17, which is a fractured test piece from the bar shown in Fig. 13, and from a contiguous portion. The history of the metal represented in Fig. 17 is:

Roll 2$\frac{1}{16}$ to 1.040 in.
Anneal ½ hr. at 700°C.
Roll 1.040 to 0.625 in.
Anneal ½ hr. at 625°C.

The only difference in the mill treatment of the two specimens (Figs. 13 and 17) was in the first mill anneal, the former being at 425°C., the latter at 700°C. This difference has been sufficient to remove every appearance of unsoundness in Fig. 17, which shows a metal with a fine, "silky" fracture without any notches or protuberances of the sort seen in Fig. 13. In short: the phantoms have disappeared by reason of a single anneal at 700°C.

Here again, the authors do not wish to be specific regarding the time and temperature necessary to effect this result. It depends on too many factors. It is only claimed that such time and temperature are within the limits of commercial practice.

CONDITIONS UNDER WHICH PHANTOMS OCCUR

While phantom laminations do not represent unsoundness of a degree that can be detected with the ordinary microscope on polished and etched surfaces, they occur in the portion of a bar that was of less than maximum density at the time of casting. Commercial brass castings in the alloy range that has a temperature gap between liquidus and solidus are subject to interdendritic unsoundness in the central regions. Genders and Bailey* have described this, illustrated it with etched sections, and discussed its causes, which are implicit in the mechanics of solidification. It is a well recognized condition.

Briefly, in the process of filling a mold, the last region to freeze is cut off from free access to an adequate supply of "feed

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* Genders and Bailey: Casting of Brass Ingots, 18, 52, 53, et seq.

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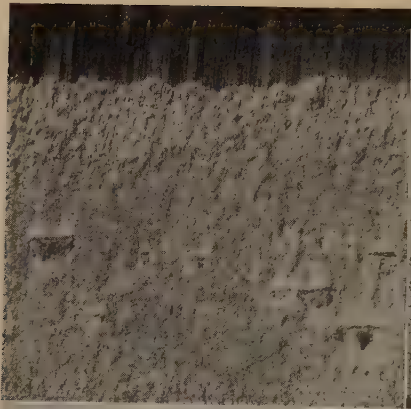

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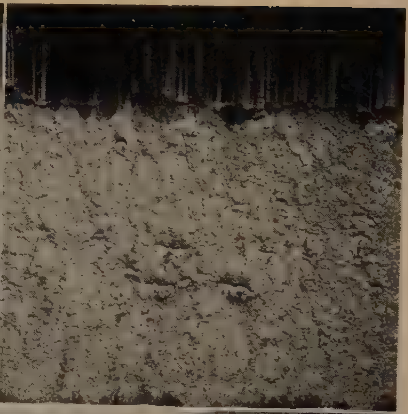

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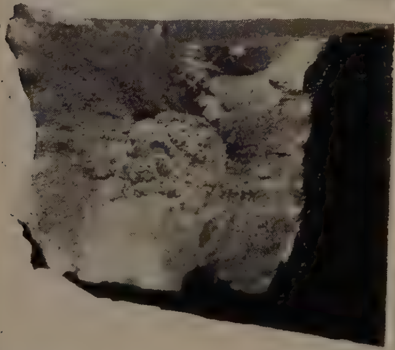

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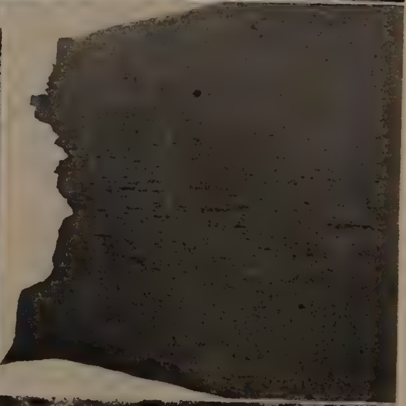

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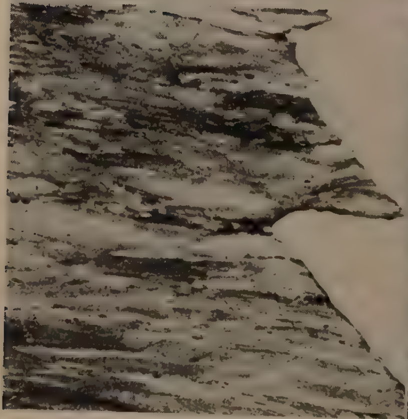

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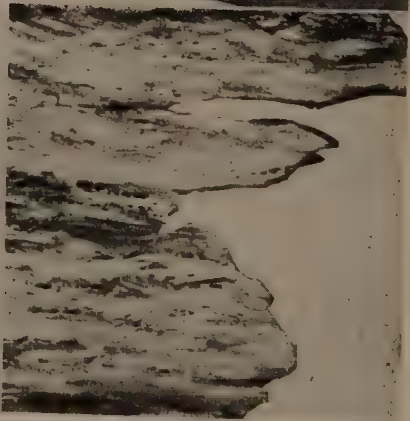

Fig. 11.—Shear cut 70-30 brass, cold-rolled and annealed briefly at 600°C. × 2.5.

Fig. 12.—Shear cut 70-30 brass, cold-rolled and annealed twice. Anneals ½ hour at 450°C. × 2.5.

Fig. 13.—Tensile fracture 70-30 brass, cold-rolled and annealed twice. ½-hour anneals at 450°C. and 625°C., respectively. × 4.

Fig. 14.—Lengthwise section through fracture of tensile specimen shown in Fig. 13. × 7.

Fig. 15.—Lengthwise section through fracture of tensile specimen of cold-rolled 70-30 brass containing phantoms. × 75.

Fig. 16.—Another specimen of metal shown in Fig. 15. × 75.

metal," and some of the interdendritic interstices remain unsatisfied. The bottom end of a casting never contains interdendritic slackness. For a short distance it freezes from the bottom upward quickly enough to draw "feed metal" from above. Neither is there any interdendritic slackness at the top of a casting, if the shrink at the top is continuously fed with fresh, hot metal until solidification of the whole bar is complete. For obvious reasons, the edges of a casting are not subject to interdendritic unsoundness. They freeze first and feed from the central portions.

It is significant that phantoms occur only in that portion of a bar that is liable to interdendritic unsoundness. They are not found at the extreme ends nor close to the edges of a strip. If the assumption is valid that phantoms are associated with unsoundness of the interdendritic type, they should be absent in a casting that contains no such unsoundness. The obvious condition for accomplishing this—i.e., freezing from the bottom up—offers difficulties in commercial application. But a very sound casting can be made if it is quite shallow. In practice this implies "edge pouring." Such a bar might be, for instance, 24 in. wide by 5⅝ in. thick by 9 in. high. The 2:1 alloy cast in this mold and hot-rolled has never shown any phantoms.

Central slackness can also be modified in a casting of considerably greater height to thickness ratio by the use of a well-made hot top that will hold a substantial amount of hot metal for feeding purposes until all the metal in the mold is frozen. Experimentally this was done with a mold 16 in. wide by 4⅜ in. thick by 19 in. high. A hot top composed of any of the very light insulating bricks commercially available was used as a superstructure, extending about 4 in. above the mold, and holding about 75 lb. of metal. After filling the mold and hot top, the metal was covered with carbon black to prevent heat loss by radiation, and feeding was continued to keep the hot top full as metal was drawn out of it by the solidifying ingot. Under these conditions the metal in the hot top remained liquid for 10 or 15 min.—substantially longer than required for the ingot proper to freeze completely.

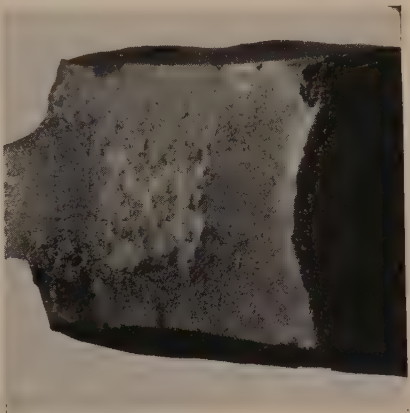

Fig. 17.—Same metal as in Fig. 13, but annealed at 700°C. and 625°C. × 7.

This was not a practical way to make brass, but was done by way of exploring the condition under which phantoms are found. The 2:1 alloy made in this mold by ordinary routine, without the hot top, was invariably infested with phantoms, but in repeated trials it never contained any phantoms when the hot top was used as described. It was, however, necessary to do a thorough job. If the hot top was not made of suitable insulating material, or for any reason did not keep its contents liquid for a long time with reference to the ingot proper, it was ineffective, and phantoms were found in the metal after hot-rolling.

Interdendritic unsoundness can also be modified by the rate of pour. For instance, in a mold such as mentioned above, with a height to thickness ratio of well over 4:1, phantoms were essentially absent after pouring rate of 6.5 sec. per inch of rise (2 min. for filling a mold 18 in. deep), which is about half the normal rate for a mold of this sort. This is not a sure method and in practice involves complications. It is cited to indicate that anything that modifies interdendritic slackness has a modifying effect on phantoms.

The same is true of cold-rolled metal. Using the water-cooled mold, which requires a rather liberal oil dressing, 2 sec. per inch of rise is about the slowest pouring rate that has been consistent with clean castings, as to surface. Anything much slower than that is likely to result in dirty castings. In a casting 2⅛ in. thick by 56 in. high, one would hardly hope to prevent slack center entirely. But by varying the pouring rate from 1 sec. to 2 sec. or more per inch of rise in the mold, the slackness can be modified over a considerable range. Large numbers of samples examined after the breakdown anneal (rolled from 2⅛ to 1.040 in. and annealed) indicated that the degree of phantoms corresponded to the rate of pour. The slower the pour, the fewer the phantoms; and the fewer the phantoms, the more readily they are absorbed. This has been observed on a large scale and is, for that matter, a recognized principle of routine practice.

Reference to phantoms in hot-rolled brass has, up to this point, purposely been confined to 2:1 alloy. We were working with it at the time they were first recognized and it was an excellent medium for their study. Any commercial bar of 2:1 contained plenty of phantoms if sheared after hot-rolling, but they were not believed to occur in 70-30. However, as work with artillery cartridge cases got under way, it became apparent that phantoms were sometimes present in the hot-rolled bar; sometimes absent. It was a common observation that a given bar either showed phantoms throughout its whole central length or it was entirely clear. This pointed to some unknown variable, which was not at once identified. It was puzzling that, in a given lot of metal anywhere from 5 to 75 per cent of the bars should contain phantoms. It was possible to absorb them with suitable mill work after hot-rolling, but it was not possible to produce them by varying the hot-rolling temperature. And we were never able to go into the casting shop and say: "by doing thus or so we will make castings that contain phantoms"—we knew of some conditions that would prevent them, but all attempts to produce them at will were futile. They might appear, or might not. There was no rhyme or pattern to the results until it was realized that alloys with more than about 71 per cent copper never contained any phantoms; with less than 70 per cent copper, phantoms were general. The dividing line is fairly sharp and not far from 70.5 per cent. Since cartridge brass was made within the limits of 68.5 and 71.5 per cent copper, and the great bulk was between 70 and 71 per cent, the spotty and irregular occurrence of phantoms in hot-rolled metal became obvious.

In brass that has been broken down cold, phantoms are not limited to this range of composition. They have been found in metal at least as rich as 85 per cent copper, 15 per cent zinc. The cold breakdown is not ordinarily used on metal more than about 2¼ in. thick, and the first anneal for the alloys under discussion occurs after a reduction of about 50 per cent. At this point phantoms are quite universal, but it should be said that the best place to look for them is in metal from castings of substantial size. With thin, light castings they might be pretty well obliterated even in the first anneal.

Discussion of Results

The observed fact that phantoms are not found in the hot-rolled copper-zinc alloy containing more than about 70.5 per cent copper leaves us with scant clue to the reason. So far as this paper is concerned, it will have to be left that way. There is, certainly, no break in the tendency to interdendritic unsoundness in that region.

If that is the cause of phantoms in 2:1 alloy, the reason for their sudden disappearance between 70 and 71 per cent copper is not clear. The only change known to occur with the increase of copper through this range is the disappearance from the castings of the last traces of beta.

In the early stages of the work it was recognized that phantoms were associated with beta. Tracing them back from a sheared face, they characteristically ended in a beta string, as in Fig. 5. But, while phantoms are generally associated with beta, the converse is not true. The very sound 2:1 castings from shallow molds, which had no phantoms, contained plenty of beta. Even the edge and end portions of commercial 2:1 castings, where phantoms are never found, contain beta in quantity. It can be said, then, that phantoms after hot-rolling have been found only in regions where interdendritic unsoundness occurred simultaneously with beta.

The authors take the view that phantoms represent inhomogeneous areas where variations in concentration have fractured selectively. Since any casting is known to be inhomogeneous until it has had a considerable amount of mill work, one need only consider how much work is required to effect homogeneity, in a commercial sense. In the range from 65 to 70 per cent copper, it appears that ordinary hot-rolling is not sufficient to homogenize the areas of interdendritic slackness. It makes little difference whether the interstices tend to inhibit diffusion, or whether such areas are less homogeneous than others, or both. The phantoms in hot-rolled alloys of this range are an observed fact. It is also an observed fact that they do not appear in hot-rolled metal of more than about 71 per cent copper. Whether beta is a factor in the result, or merely coincidental, is not beyond question. We can only observe that some change in character occurs by virtue of which the richer alloy is homogenized in ordinary hot-rolling while the poorer alloy is not. This does not place too great a strain on the imagination, and absence of phantoms in the sound portions of any of the castings under discussion inclines us to the view that beta is merely coincidental.

It is not strange that phantoms in cold-rolled metal are not limited by the same composition range as in hot-rolled metal. The former, involving, perhaps, four or five passes and a reduction of 50 per cent, could hardly be expected to effect the diffusion that might occur in the latter, which might involve 10 or 12 passes and a reduction to a tenth of the original thickness, all at a temperature at which grain growth occurs. It is more surprising that such treatment fails to accomplish absorption of phantoms in all alloys. The reason, perhaps, lies in the time factor, which, in hot rolling, is short. It has been shown that short anneals at low temperature are ineffective in treatment of phantoms but that in hot-rolled metal they disappear if followed by a substantial anneal plus a single cycle of cold-rolling and annealing. In cold-rolled metal, they disappear in the second cycle of rolling and annealing if the first anneal has been substantial and reasonably sustained. It all fits the assumption that diffusion is the controlling factor.

Throughout this presentation the terms "interdendritic unsoundness" or "slackness" have been used interchangeably for lack of better terms to designate a condition which we have maintained is not unsound after mill work. We are aware of the seeming anomaly, but believe there will be no misunderstanding, since a low density at the center, resulting from contraction of volume on solidification, does in fact consolidate and heal so that no cavities resulting from it can be found under a microscope. Having said this, we wish at once to qualify it. It is not our intention to give carte blanche to all degrees of contraction cavities. That would cover a subject and a range outside the scope of this paper. We particularly wish to avoid reference to cavities of any other nature. They are not under discussion. We refer only to the well-known interdendritic interstices that are inevitable in commercial methods of brass casting.

Summary and Conclusion

In the early stages of mill work, brass sometimes has, in a sheared section or tensile fracture, the appearance of countless laminations which, in fact, do not exist as such. They are the result of selective fracture in metal that has not been sufficiently homogenized by mill work, and disappear after one or more additional cycles of rolling and annealing. The shear cut or fracture is then smooth and silky, with no suggestion of unsoundness. The appearance of laminations is so convincing and their disappearance so complete that they have been called phantoms. Phantoms have been observed in hot-rolled brass of 65 to 70 per cent copper, but not of more than 71 per cent copper. In cold-rolled brass they cover the same range, but are not limited to 70 per cent copper. Phantoms occur only in the central portion of a bar which, as cast, contained interdendritic interstices due to contraction of volume in freezing.

While the phantom does not necessarily imply inferior quality, it has caused wide and merited concern to the brass-manufacturing industry. Since it is not possible, in routine inspection, to distinguish it from an actual cavity, flattened in rolling, it has frequently been the basis of rejection. Effective methods of controlling phantoms have been indicated.

Acknowledgments

Acknowledgments are due the American Brass Company for permission to publish; to many members of the staff, and particularly to Messrs. Earl Palmer, F. N. Meyer and Hollis Poore, for cooperation and assistance.

DISCUSSION

J. Rae, Jr.*—I have read this practical paper with great interest, and although I have no experience in rolling-mill practice it may be of interest to record that we have encountered similar "phantom laminations" in extruded rods.

We investigated this matter several years ago and found that these "apparent defects," as we termed them, appeared in rods from time to time and were nearly always confined to the front half of the extruded bar. The trouble was most frequently encountered in manganese bronzes (57 to 60 per cent copper) but also, on occasions, in commercial-quality free-machining rod. We found further that the defects took several forms—sometimes a laminated discontinuous structure, as illustrated by the authors, and sometimes distinct cracks. Investigation revealed that the form of the apparent defect was usually governed by the method of fracture, and this led us to carry out the following series of tests.

We first took a 1¼-in. dia. manganese-bronze rod which showed the apparent defect from the front end, extending to half the length of the extrusion. A portion was partially cut through on a rotary-type cutter and fractured. The fracture showed a very obvious lamination. An adjoining piece was then sawed one third through on a saw bench and fractured. This time the lamination appeared running in a different direction to the previous fracture. Another adjoining piece was fractured in a vice after being hack-sawed on each side. The fracture this time showed discontinuous laminations of a quite different appearance to the previous fractures.

For the second series of tests these three portions of bar showing the apparent defects in the fractures were machined, polished and microscopically examined in order to ascertain whether the defects or laminations extended appreciably below the fractured surface and whether they were in fact present in the bar. After "skimming up" the fractures in a lathe and polishing the cross section, slight cracks were visible, but on removing about ⅛ in. of metal and repolishing they were found to have disappeared, and no flaws could be seen under the microscope. Similarly, after longitudinal sections had been polished, the laminations were found to be only about ⅛ in. deep, the metal below this being quite sound.

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* Chief Metallurgist, McKechnie Brothers Ltd., Birmingham, England.

Next, a series of pressure tests was carried out on what appeared from the fracture to be very unsound rod. Hollow cylinders, ¾ in. i.d. by 1½ in. o.d. with ⅛-in. base thickness, were machined from the rod and similar cylinders were machined from a scrap back-end portion of similar rod showing the extrusion defect. Oil at 4500 lb. pressure per square inch was applied to the inside of these cylinders and while the oil penetrated through the extrusion defect in the samples made from back end rod, the samples made from rod with the apparent defect passed the test satisfactorily. The bases of the satisfactory cylinders were then reduced to 1/16 in. thickness and oil was applied again, at a pressure sufficient to cause the bases to bulge. Again, none of these samples showed any leakage.

A few tests were carried out which further demonstrated that the apparently unsound rod was in fact quite sound, although, on the appearance of the fractures, an inspector would not pass the material.

Various tests were then carried out involving variations in extrusion conditions, such as temperature and speed of extrusion, but none of these tests threw any light on the subject.

The conclusions we reached were that the apparent defects or laminations were caused by the tearing action or pulling apart of the grain fibers during fracturing and that in instances where this occurred the density or strength of the metal was not homogeneous. Like the authors, we traced the origin of the trouble to the foundry, the fact that the defects occurred more frequently with manganese bronze than with other alloys being a pointer in this direction.

It is of interest to note that these "defects" were rarely encountered in the back halves of extrusions, possibly because the greater amount of hot-work has the effect of reducing these variations in density.

D. R. Hull, H. F. Silliman and J. R. Freeman, Jr. (authors' reply).—Mr. Rae's comments are pertinent and open the subject to a wider range of speculation than the authors have had the temerity to suggest. The condition that he observes in manganese-bronze rod has, locally, been referred to as "woody structure." We see no reason to doubt that it is related to phantoms in cartridge brass if not actually the same thing. Woody structure is also found in aluminum bronze under conditions that point toward dissolved gas as a cause, although no unsoundness can be detected. While, as manufacturers, we are inclined to be satisfied with methods for controlling these phenomena, such control does not always throw much light on the real cause. It is felt that before these apparent defects are fully explained some rather fundamental work will have to be done, which will probably lead us farther than is now apparent. Therein lies the justification for writing about them.

Corrosion of Yellow Brass Pipes in Domestic Hot-water Systems—a Metallographic Study

By E. P. Polushkin,* Member A.I.M.E., and Henry L. Shuldener†

(New York Meeting, February 1945)

This paper describes the results of microscopic examination of a series of brass pipes removed from apartment and office buildings in New York City, adjacent localities on Long Island, and Philadelphia. They were selected as typical of approximately four hundred pipe specimens obtained over a period of five years during an investigation of corrosion in hot-water installations. A part of the investigation is reported in this paper and includes a brief history of the pipes, a description of their inside surface and microstructure, and a study of the effects of corrosion, with particular reference to the structural aspects of local and selective dezincification.

Although the bibliography on the corrosion of brass pipes is quite extensive, it refers almost entirely to corrosion in sea water. The authors believe that their examination of this series of pipes, which had been subjected to the corrosive action of fresh water for various lengths of time, may throw some additional light on the problem of corrosion.

Pipes Examined

The pipes were made by different manufacturers and their sizes range from ¾ in. to 4 in. nominal inside diameter, the majority being within 1 to 2 in. They can be divided into two groups according to chemical composition: (1) with a copper content of 60 to 62 per cent and (2) with a copper content of 65 to 68 per cent. The first group (pipes made of Muntz metal) comprises 22 pipes and the second (pipes made of high brass) comprises 18 pipes.

The pipes had been in service in various locations in the hot-water systems of the buildings involved. Some were taken from horizontal lines in the basement, some from overhead distributors and some from vertical risers. The distance, in terms of feet of pipe, of the specimens from the hot-water generator was no less than 75 ft. and often 100 to 300 ft. In the majority of cases the water-heating equipment was provided with a regulator to limit the temperature of the hot water supply. The normal range of temperature in pipe systems of this kind is 100° to 160°F.

Water Supplies

The average chemical composition of the water supplies carried by the pipes is shown in Table 1. In evaluating the corrosiveness of a natural water, four factors are considered of prime importance: namely, hardness, alkalinity, pH and silica content. The waters listed in Table 1 are characterized by relatively low hardness, low alkalinity, low pH and low silica content. The waters of lower pH and higher CO_2 content are more corrosive. A characteristic of all of these waters is that they do not deposit a protective mineral coating as do waters with high bicarbonate of lime content, which would be reflected

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† Chemical Engineer, President and Technical Director, Water Service Laboratories, New York City.

in water analyses as high hardness and high alkalinity. Therefore, the inside surfaces of pipes through which these waters flow are exposed to the corrosive attack of the free oxygen and carbon dioxide dissolved in the water.

TABLE 1.—*Typical Analysis of Municipal Water Supplies*[a]

	New York City	Jamaica, L. I.	Rockaway, N. Y.	Philadelphia
Total hardness as $CaCO_3$	31	70	28	56
Calcium hardness as $CaCO_3$	15	38	15	34
Magnesium hardness as $CaCO_3$	16	32	13	22
Total alkalinity as $CaCO_3$	24	30	9	24
Free carbon dioxide as CO_2	2	12	13	2
Chlorides as Cl	2	17	8	5
Sulphates as SO_4	8	40	8	30
Silica as SiO_2	3	13	10	5
pH	7.2	6.7	5.9	7.0

[a] All figures parts per million except pH.

The oxygen content of the waters involved was about 80 per cent of saturation for atmospheric pressure and the temperature of the cold water entering the hot-water systems.

LENGTHS OF SERVICE OF PIPES

The lengths of service of the pipes examined are given in Table 2. It should be noted that these figures do not necessarily express the full service life of the pipes because most of the pipes were removed for the purpose of our examination without consideration of whether they were still serviceable. Moreover, some sections of pipe, practically unaffected by corrosion after relatively long service, are not always typical of the entire piping system of the building. In other words, it was not unusual to find some specimens in a building badly dezincified and other adjacent or near-by sections in sound condition. It should also be noted that the actual service life of the pipes is controlled by local corrosion (plug type), the rate of which is so much more rapid than that of general corrosion that pipe walls are completely pierced before general corrosion has proceeded very far (Table 2, pipes 5, 50, 54, 66, 70, 93, 101).

MINERAL DEPOSITS

The inside surfaces of all pipes were covered with a mineral deposit, which usually had a distinctive color. Below this there was a layer of cuprous oxide (sometimes discontinuous) directly bound with the underlying metal. The cause of this superficial oxidation was of interest, and in order to explain it several new pipes were examined. Only traces of oxide were found on their inside surfaces and further examination of the used pipes proved beyond doubt that the oxide layer had been caused by corrosion during their service.

Surface imperfections such as small cracks, grooves or pits were often found below the mineral deposits. Although some of these defects were insignificant from a general viewpoint, they should be considered a possible cause of incipient corrosion because they can induce it or accelerate its action.

In some pipes the oxide layer was not found, but the metal was covered with a grayish black film, which protected the metal from oxidation (pipes 61 and 65). This was evident from the condition of bare spots, which had been attacked by corrosion where the film had been broken off. This film might have been formed during the manufacture of the pipe or in the early stage of service, as the result of water action.

A few unsuccessful attempts were made to determine mineralogical composition of the deposits. They all failed because not enough powder could be scraped from the pipe surface.

MICROSTRUCTURE OF PIPES

Specimens for microscopic examination were usually polished in two perpendicular

TABLE 2.—*Pipes Examined*

Pipe No.	Size of Pipe, In.	Metal	Water Supply	Location of Pipe	Years in Service	Structural Constituents	Grain Size, Microns	Maximum Depth General Corrosion, Microns	Tubercles and Plugs
5	1	Muntz metal	New York	Main horizontal feed	10	Alpha and Beta	50	75	Many tubercles. Wall pierced
7H	¾	Muntz metal	New York	Horizontal return	8	Alpha and Beta	50	100	Plugs up to 1000 microns. Many tubercles
9	¾	High brass	New York	Horizontal return		Alpha	70		
11	1	High brass	New York	Horizontal return	2½	Alpha	60	60	Small tubercles
13	¾	Muntz metal	New York	Vertical return	13	Alpha and Beta	70		
16	1½	Muntz metal	New York	Horizontal overhead, 32d fl.	8	Alpha and Beta	50	50	Large tubercle
17	2	Muntz metal	New York	Vertical riser, 14th fl.	11	Alpha and Beta	50	60	Very small tubercles
24	¾	High brass	New York	Vertical branch	13	Alpha, Trace Beta	60		Rows of very small tubercles
31	1½	High brass	New York	Main horizontal feed	2½	Alpha	60	75	Large and small tubercles
39	¾	Muntz metal	New York	Main horizontal feed	11	Alpha and Beta	50	215	
50	1¼	High brass	New York	Main horizontal feed	3	Alpha	30–60 and larger	400	Many tubercles. Wall pierced
53	2½	High brass	New York	Main horizontal feed	13	Alpha	150–200	100	See text
54	1¼	Muntz metal	New York	Horizontal return	7	Alpha and Beta	50	300	Wall pierced
58	¾	Muntz metal	New York	Horizontal return	12	Alpha and Beta	120	100	
61	1½	Muntz metal	New York	Horizontal supply	11	Alpha and Beta	50	200	Many small tubercles
62	1¼	Muntz metal	New York	Horizontal return	11	Alpha and Beta	80	50	Large tubercles
65	¾	Muntz metal	New York	Horizontal return	10	Alpha and Beta	50	170	Small tubercles
66	1½	High brass	New York	Horizontal supply	12	Alpha	Uneven some 500	100	Wall pierced
67	¾	High brass	New York	Horizontal return	11	Alpha and Beta	80	150	
70	1½	Muntz metal	New York	Horizontal return	11	Alpha and Beta	450	75	Wall pierced
73	1	Muntz metal	Jamaica	Horizontal return	11	Alpha and Beta	120	210	Small tubercles
73A	1	Muntz metal	Jamaica	Horizontal return	11	Alpha and Beta	100	Layer corrosion	Badly corroded. Several large tubercles
93	1	High brass	Rockaway	Vertical riser	7	Alpha	80–100	Layer corrosion	Badly corroded. Wall pierced
101	2	High brass	Rockaway	Horizontal overhead	7	Alpha	Av. 100	Layer corrosion	Badly corroded. Wall pierced
104	2	Muntz metal	New York	Horizontal return	16	Alpha and Beta	50	220	Numerous small tubercles
116	1	High brass	New York	Horizontal feed	9	Alpha	70	130	Incipient tubercles
117	3	High brass	New York	Horizontal feed	13	Alpha	100	350 not uniform	Numerous small tubercles
118	1	Muntz metal	New York	Horizontal return	9	Alpha and Beta	50	280	
119	1	High brass	New York	Horizontal return	8½	Alpha	75	Layer corrosion	
120	1½	High brass	New York	Horizontal supply	13	Alpha	100	170	
125	¾	Muntz metal	New York	Horizontal supply	8	Alpha and Beta	50	300	Numerous plugs
129	4	Muntz metal	New York	Horizontal overhead	25	Alpha and Beta	50	100 top 340 bottom	Many incipient tubercles
132	1½	High brass	New York	Horizontal overhead	20	Alpha	100–110	200	
133	1¼	Muntz metal	New York	Horizontal return	9	Alpha and Beta	60	170	
134B	¾	High brass	Philadelphia	Horizontal branch	9	Alpha	60	1650	Numerous large tubercles
149	1	Muntz metal	New York	Horizontal branch	7	Alpha and Beta	50	480	Small tubercles
155A	1½	Muntz metal	New York	Horizontal overhead 32d fl.	9	Alpha and Beta	50	50	Unusually large tubercles
155B	1½	High brass	New York	Horizontal overhead 32d fl.	1½	Alpha	70–75	20	
200D	¾	High brass	Philadelphia	Horizontal supply	1	Alpha	175	540	Numerous small tubercles
233	1	Muntz metal	Philadelphia	Vertical riser	9	Alpha and Beta			Large tubercles

sections, longitudinal and transverse, but for examination of advanced corrosion at the root of plugs, a tangential section (parallel to geometrical axis of pipe) was also prepared. The specimens were examined before and after etching. Two etching reagents were generally used: (1) ammonium hydroxide with addition of a few drops of hydrogen peroxide and (2) aqueous solution of ammonium persulphate. In the routine etching of alpha-beta brass it was sufficient to bring out the two constituents, but in some cases, where the structural peculiarities of alpha grains required development, a deeper etching with the same reagents was applied.

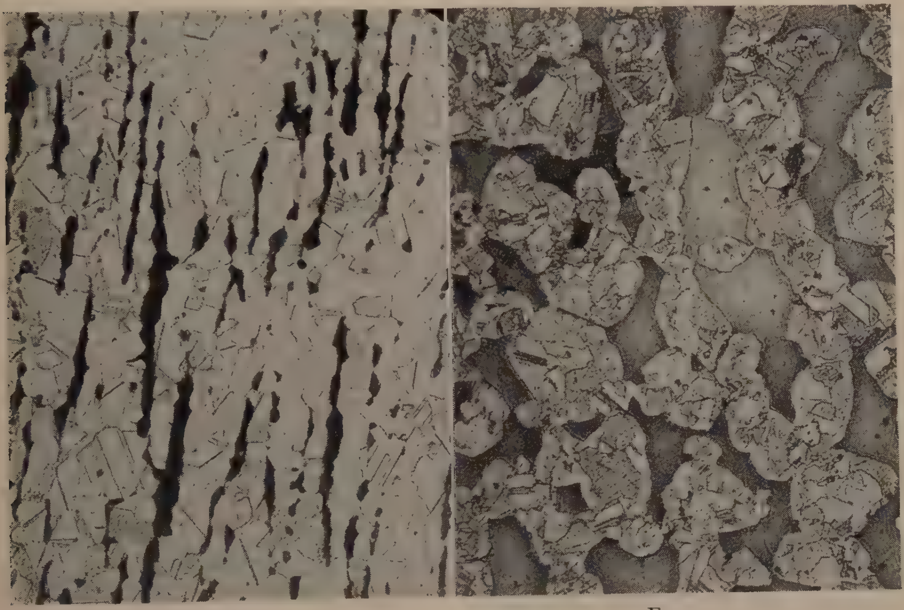
Fig. 1. Fig. 2.

Figs. 1 and 2.—Muntz metal. × 200.
Fig. 1. Longitudinal section. Pipe No. 17.
Fig. 2. Cross section. Pipe 73-A.

Polished sections containing large accumulations of metallic copper required a special etching method. Small droplets of ammonium persulphate solution were placed at different points within the area of the copper deposit, one after another at certain intervals, so that the time of etching was different at these points. After the reagent had been washed off and the specimen dried, the etched spots were examined and compared. In this manner a proper degree of etching was determined without a repeated repolishing and re-etching of the whole section. This method was used for examination of the microstructure of the copper deposits that had been formed by corrosion.

The distinctive features of the microstructure of the pipes were directly related to their chemical composition and conditions of processing. Twenty-two pipes were made of Muntz metal and 18 of high brass. The first alloy contains two solid solutions, alpha and beta; the second, only alpha. The proportion of beta in pipes made of Muntz metal varied according to the zinc content, which in industrial alloys of this type ranges from 37 to 41 per cent, and, to a certain extent, according to the rate of cooling from the temperature of the last operation of hot work. In some pipes of the alpha-beta group (16, 17, 39, 67, 118 and 113) the amount of beta was found to be considerably below the normal proportion. For the same reasons a trace of beta was found in one pipe of the alpha group (No. 24).

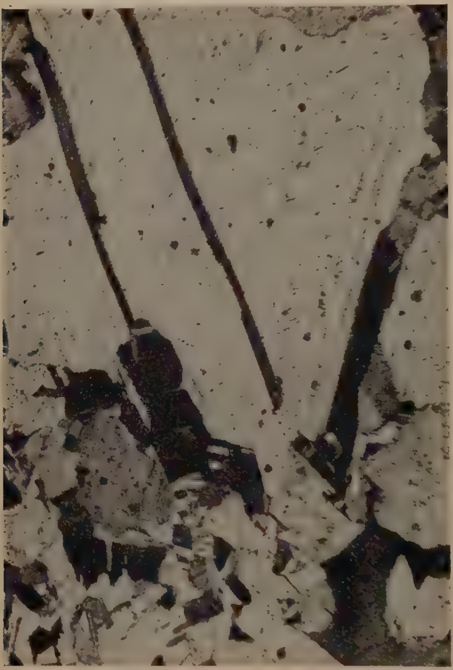

FIG. 3.—INHOMOGENEOUS GRAINS OF ALPHA, PIPE NO. 66. × 200.

Typical views of the microstructure of alpha-beta brass pipes are shown in Figs. 1 and 2, which represent, respectively, longitudinal and transverse sections of pipes 17 and 73*A*. In both photomicrographs beta appears dark. Although both pipes were made of Muntz metal, the difference in the amount of beta is very pronounced.

The following deviations from the normal structure were found occasionally:

1. Coarse primary structure, not entirely eliminated by annealing, as evidenced by Widmannstätten pattern of alpha and beta arrangement.
2. Striking variations in grain size (Fig. 3).
3. Distorted shape of grains and presence of slip bands, which indicate insufficient annealing.
4. Inhomogeneous distribution of beta.

These defects were not common, but are mentioned only for a better understanding of all the conditions that may promote or influence corrosion.

Grain size was determined by measuring the diameter of major sections of grains by means of a micrometer eyepiece, and also by the direct comparison of the grain size with the standard photomicrographs of American Society for Testing Materials. The values of grain size in microns are shown in Table 2.

As shown in this table, 15 pipes had the smallest grain size of 50 microns; in the majority of pipes (28) it was from 50 to 80 microns; in 10 pipes, from 100 to 200 microns, and in two pipes, from 450 to 500 microns. One of the last two pipes had Widmannstätten structure and the other had exaggerated grain growth.

These figures of grain size should be divided by 2 if it is desired to compare them with the mean values of grain size as usually determined by the ordinary methods.

DEFINITION OF TERMS

The term *general corrosion* is taken to mean the corrosion of the whole inside surface of the pipe, or at least a large part of it.

Local corrosion—i.e., *plug-type corrosion*—refers to a destructive attack concentrated at a specific point only, the rest of the surface remaining intact or being attacked at a much lower rate.

Other terms mentioned in this paper in connection with corrosion are defined for the sake of clarity, as follows:

"Layer-type" corrosion refers to a copper deposit that extends over a large area and

shows stratification and porosity of the kind generally found in the plug type. It may be considered as a plug extended over a large area. Often corrosion advances so rapidly at some points in the layer that typical semicircular plugs are developed, which penetrate into the wall of the pipe.

In all three terms, the meaning of "corrosion" includes the entire cycle of processes of corrosion; viz., dezincification as well as subsequent oxidation of copper.

Selective dezincification refers to a process of which a singular feature is the selective removal of zinc from the alpha or beta constituents.

Preferential attack is used to designate the order of destruction of structural constituents. In alpha-beta brass pipes, beta is always corroded first. Another instance of preferential attack is found in old bronzes, where either alpha or eutectoid is attacked first.[20]

General Corrosion

Microscopic examination showed that all pipes examined had been attacked by general corrosion, the difference between individual specimens being only in the depth of penetration. It was also revealed that the process of corrosion in alpha-brass pipes had advanced in two steps: first, alpha was destroyed and replaced by metallic copper, then the copper was oxidized. Examination of longitudinal and transverse sections indicated that at the advanced line of corrosion little or no cuprous oxide was found. However, as the inside surface of the pipe was approached an increasing amount of cuprous oxide was found, but almost no copper. Since a layer of cuprous oxide was always found below the mineral deposit, we must conclude that it was the last product of corrosion.

A second layer of more recent origin, at the advance line of corrosion in contact with the normal structure, consisted of copper and cuprous oxide. In one pipe (No. 11) copper deposit was not found; there was only oxide and alpha. However, it seems likely that the absence of metallic copper was due to rapid oxidation of the copper into oxide, as soon as it had been formed.

General corrosion of the constituents in alpha-beta brass pipes also took place in two steps, as described above, but its distinctive feature was in the preferential attack of beta. In extreme cases, as in pipe 54, beta was destroyed throughout the whole thickness of the wall while alpha remained completely unaffected. On the other hand, in some pipes the lag between the attacks on beta and on alpha was short.

The depth of general corrosion was determined on longitudinal or transverse sections of pipes by direct measurement under the microscope. The values of depths given in Table 2 represent the maximum penetration of corrosion, which is the sum of the maximum widths of both layers; i.e., (1) cuprous oxide alone and (2) cuprous oxide plus metallic copper. In alpha-beta brass pipes these figures give the maximum depths of preferential attack on beta.

As the pipes were in service for different periods of time, the only possible way of comparing the rates of their general corrosion was on the basis of mean values of the depths of corrosion per year. Table 2 shows that the rate was very slow in a great majority of the pipes. Of 32 pipes in which the depth of penetration was determined, the rate was $\frac{1}{40}$ mm. per year in 23 and $\frac{1}{40}$ to $\frac{1}{20}$ mm in 5. Only in one pipe was it slightly over $\frac{1}{2}$ mm. per year. This pipe (200D) was from Philadelphia and in one year of service developed general corrosion 540 microns deep. Table 2 also indicates that there is no relation between grain size and the depth of corrosion.

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[20] References are at the end of the paper.

Local Corrosion

The destructive action of this type of corrosion is concentrated on a single point of the surface, which is vigorously attacked.

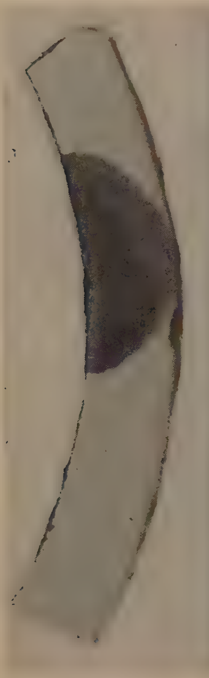

Fig. 4.

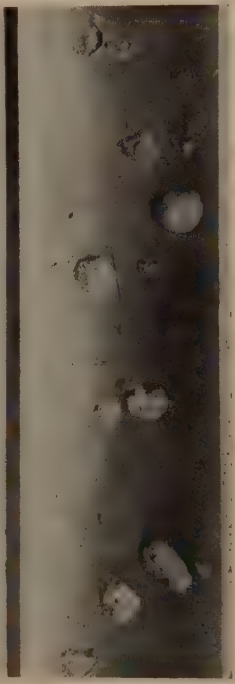

Fig. 5.

Fig. 4.—Plug in pipe 66. × 3.
Fig. 5.—Tubercles in pipe 5. Natural size.

As in general corrosion, the process involves removal of zinc and formation of a copper deposit, which then becomes partially oxidized. A large local accumulation of copper in the pipe wall is commonly called a "plug," as it often extends through the entire wall thickness (Fig. 4). The mound built up by the products of corrosion on the inside surface of pipe above the plug is generally referred to as a "tubercle" (Fig. 5).

Three types of plugs were found in brass pipes: (1) with all the original metal dezincified, (2) with only beta dezincified and alpha intact, and (3) plugs similar to the first type but which had developed from a layer of corrosive products (Fig. 6). An ordinary plug, type 1, can be distinguished easily from the normal metal by visual examination of the pipe, whereas a plug of type 2 appears only slightly different from the surrounding metal, even in a finely polished section of the wall. The third type represents merely an advanced stage in the layer corrosion.

Local corrosion was very common in the brass pipes examined, both alpha and alpha-beta brass being susceptible to that kind of attack. The number of large tubercles found in badly corroded pipes was as high as 20 in a 3-in. length of pipe and their size sometimes reached $1\frac{3}{16}$ in. in length and $\frac{1}{2}$ in. in height.

All plugs of types 1 and 3 consisted of porous accumulations of copper mixed with some mineral products of corrosion. Figs. 6 and 7 show sectional views of two plugs, which display dark and light concentric zones. Microscopic examination proved that the difference between the zones was mainly in the number and size of holes. In the dark zones porosity was greater and the holes were larger. The alternate arrangement of zones indicates a certain periodicity of the corrosion process. Apparently, the infiltration of a corrosive liquid through the spongy copper had been going on continuously, but with different intensities, and the dark zones were formed during the most vigorous periods of corrosion, when even a part of the copper had been removed.

The outlets of plugs on two sides of the pipe wall were usually opposite each other, but in pipe 125 the wall was pierced in an oblique direction, and the visual examination of the tangential section of the wall revealed a considerable extension of the plug along the pipe length.

Microscopic examination of tubercles disclosed that they had been built up of concentric shells, which usually had different colors and often were separated by empty spaces. In a tubercle of pipe 16 the colors of shells were white and pink, and the center was hollow. The tubercles frequently had a central cavity, apparently caused by the evolution of a gas.

The size of the tubercles was sometimes disproportionately small in comparison with the size of the underlying plugs. It is evident therefore that some of the products were carried away by the water flow.

The chemical composition of tubercles is given in Table 3. The analyses were made on tubercles removed from pipes 125, 134B, 196 and 247. (The last two are not included in the list of pipes examined.) The prevailing components are zinc, combined water and carbon dioxide.

TABLE 3.—*Analysis of Tubercles*

Pipe No.	Water Supply	Alloy	Combined Water and CO_2	Composition, Per Cent			
				Zn	Cu	Fe	SiO_2
125	New York...	α and β	24.1[a]	51.7	1.7	1.7	5.3
134B	Philadelphia	α	27.8	52.1	1.6	1.2	1.6
196	New York...	α and β	26.7	53.5	1.9	1.8	2.0
247	New York...	α	23.8	51.8	0.6	1.8	4.9

[a] Combined water 16.3 per cent; carbon dioxide 7.8 per cent.

On the basis of the data in Table 3, the hypothetical mineral composition of tubercles in pipe No. 125 was calculated, as follows:

	PER CENT
Zinc hydroxide, $Zn(OH)_2$..	60.9
Zinc carbonate, $ZnCO_3$....	22.3
Cuprous oxide, Cu_2O......	1.9
Iron hydroxide, $Fe(OH)_3$..	3.2
Silica, SiO_2...............	5.3
Combined water, H_2O.....	4.8
	98.4

Zinc hydroxide is white or yellowish and zinc carbonate is colorless; both are soluble, but only in minute quantities in water.

The yellow coloration of tubercles, and especially of the deposits on the inside surfaces of pipes, was often noticeable. A greenish tint also was frequently found, apparently caused by the presence of malachite. The amount of cuprous oxide in the tubercles was small. Iron and silica were deposited from the water.

The layer type of corrosion was found in three pipes (73A, 93 and 101) removed from buildings in localities where the water is more corrosive than in New York City. The structural characteristics of these copper deposits—porosity and stratification—are the same as in the plug type of deposits.

The origin of local corrosion is still a mystery. In boiler tubes it has been attributed to the action of air bubbles that adhere to the wall of the tube and prevent its cooling by water, thus causing a local superheating and subsequent pitting of the wall.[19] We could not find any evidence for or against this theory in the present investigation of corrosion in brass pipes. Of course, there are essential differences in the operating conditions of boiler tubes and hot-water pipes, especially in the considerably higher temperature range of the boiler tubes.

Our observations indicated that at least in some cases local corrosion had started under the influence of residual stresses and local deformations. The evidence gathered in support of this contention can be summed up as follows:

1. Incipient plugs were found within pipe walls at the end of cracks (Fig. 8). The metal surrounding the plugs obviously had been strained before cracking.

2. The outlines of original cracks often can be traced in the center of plugs.

3. A crack was found at the root of a small plug in one of the pipes.

4. In another pipe a large number of incipient tubercles had developed within surface grooves where the metal had been deformed. These grooves originated in the pipe processing (Fig. 9).

5. A plug was found piercing the wall at an angle. Instead of developing in a

direction perpendicular to the wall, as usual, the prevailing growth of this plug extended along the pipe length. This showed the tendency of corrosion to follow the lines of straining produced by cold-drawing. A crack also was discovered in the same section.

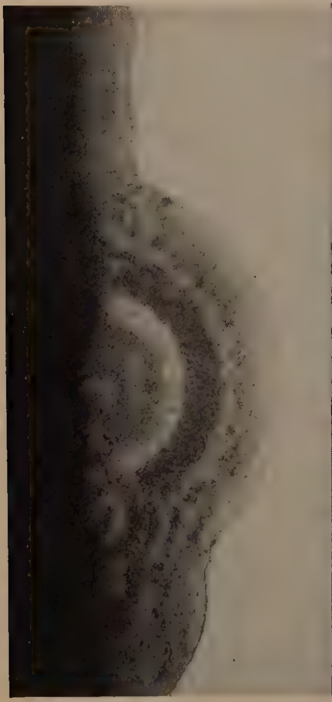

Fig. 6.

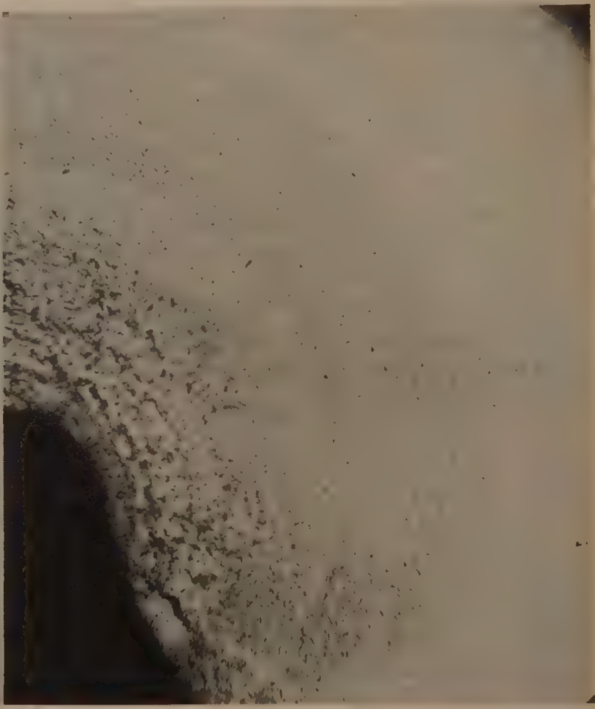

Fig. 7.

Fig. 6.—Plug developed by layer corrosion, pipe 134B. × 15.
Fig. 7.—Zonal structure of plug, pipe 93. × 25.

6. Plugs always had oval shapes in tangential sections of pipes, with the longer axis parallel to the pipe length (Fig. 10). The accelerated corrosion of the metal in the specific direction again suggests the influence of straining.

The processing of brass pipes involves cold-working, all traces of which are not always removed by the subsequent annealing. Some grains of pipes often showed a distortion of shape or presence of slip bands—a distinct proof that the stresses had not been entirely eliminated. Microscopic cracks found in the walls of some pipes are also significant (Fig. 11). As they frequently occurred in the middle of a wall section, their origin should be attributed to local stresses.

It appears certain that two or more kinds of stresses can coexist in metals. The stresses of one kind can be removed by a low-temperature annealing, but not necessarily all the stresses associated with deformation and slip. The accelerating effect of residual stresses on corrosion of metals has been pointed out by all investigators of stress corrosion.

Are Copper Deposits Residual or Redeposited?

The concept of selective corrosion of the zinc of brass was developed as early as 1903, by Milton and Larke[4] and later was supported by experimental work of Desch and Whyte.[1] They came to the

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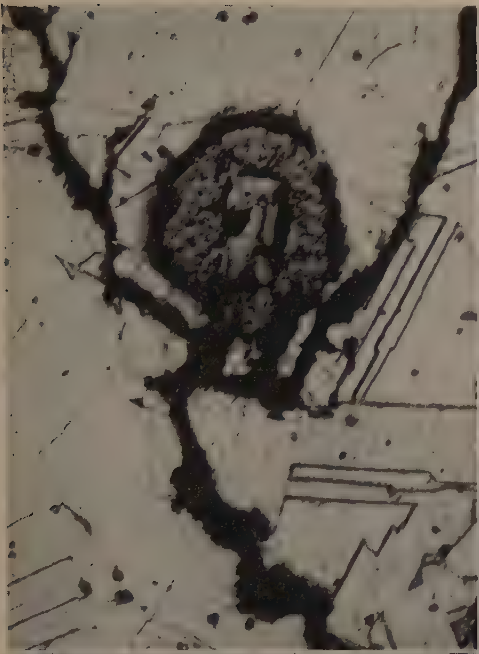

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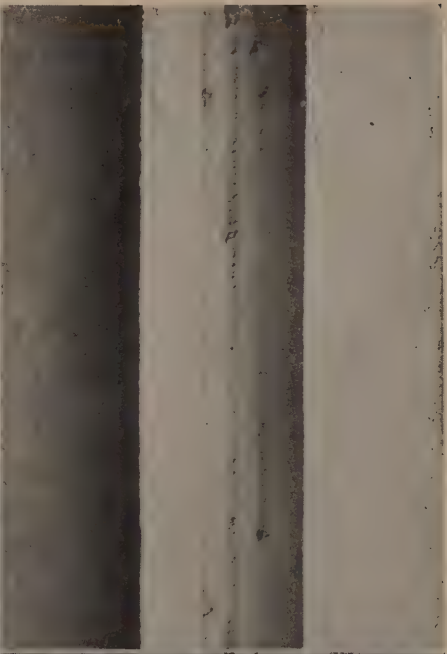

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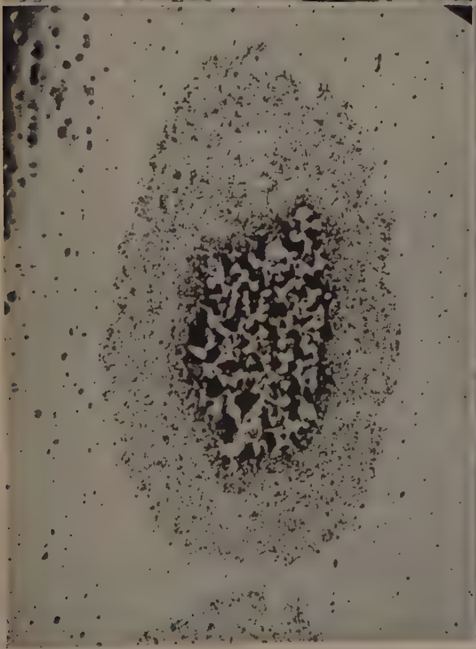

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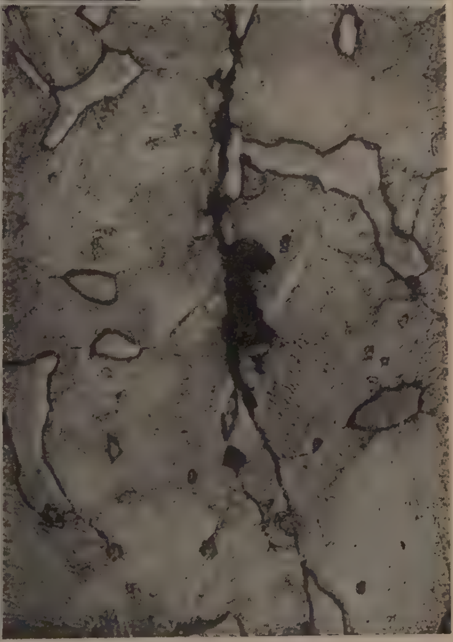

FIG. 8.—INCIPIENT PLUG AT FORK OF CRACKS, PIPE 53. × 300.
FIG. 9.—PARALLEL ROWS OF TUBERCLES, PIPE 24. NATURAL SIZE.
FIG. 10.—OVAL SECTION OF PLUG, PIPE 200D. × 30.
FIG. 11.—SLIP BANDS AND CRACK, PIPE 149. × 750.

conclusion that copper was residual. This viewpoint was suggested by some investigators of corrosion but opposed by others who believed that the copper had been dissolved and redeposited.

The authors believed that the controversy could be resolved by a microscopic study of the structural characteristics of the copper deposits. It seemed certain that if the zinc had been selectively leached out, some of the structural aspects of the original metal should still be found; as, for instance, twinning of alpha grains. On the other hand, assuming that copper had been redeposited, the microstructure of the deposits should necessarily be typical of metals precipitated from aqueous solutions. These considerations prompted the authors to study more particularly the copper deposits, especially in plugs containing large amounts of copper, which therefore offer a greater field for observations.

Dezincification of Alpha in High-brass Pipes

The search for twinning in corroded grains of alpha brass was successful. In a small plug of pipe 200D made of high brass the grains of alpha had been entirely converted into copper, yet some of them showed distinct twinning (Fig. 12*a*). The boundaries of some of these grains remained well visible. Although these grains were only a few among many others that had been merged into a solid mass of copper, apparently structureless, it was evident that the real structure of the deposits could not be observed because of the presence of minute holes. In order to obtain a proper depth of etching of the deposits in further work, "spot etching" was used as described in the preceding pages under Microstructure. Small drops of dilute solutions of ammonium persulphate in water (concentration 5 to 10 per cent) were placed on copper deposits for various periods of time. By means of this technique twinning of former alpha grains, in the deposits of other pipes (134B, 31, 101) was brought out (Figs. 12*b* and 12*c*).

Dezincification of Alpha in Muntz-metal Pipes

In the plugs of alpha-beta brass pipes, both constituents were completely replaced by copper but were not entirely merged. The "alpha" in plugs of pipes 5, 7H and 54, which were all made of alpha-beta brass, clearly showed twinning in some of the alpha grains now completely replaced by copper. In other Muntz-metal pipes examination failed to reveal it because of the porous structure of the copper. The final conclusion based on all observations was that twinning remained in dezincified alpha grains of both alloys, high brass and Muntz metal. If we assume now that copper had been redeposited, the question arises as to how the atoms of the copper could have placed themselves into the exact positions of the original grains of brass, so as to reproduce the twinning. It is known that twinning of brass grains is caused by mechanical work followed by heating. It is improbable that the pattern of the grain structure originally caused by mechanical work and heating could have been restored by precipitation of a solid from a solution, and the authors believe that the presence of twinning in the skeletons of former alpha grains is a decisive proof that the zinc had been leached out and the copper left behind.

Dezincification of Beta

In regard to the origin of copper derived from dezincification of beta, the question still remained open. In all deposits beta could be distinguished from alpha by its much darker color and by its shape. The origin of the copper could not be established by the presence of twinning, for beta does not form twins. Corrosion

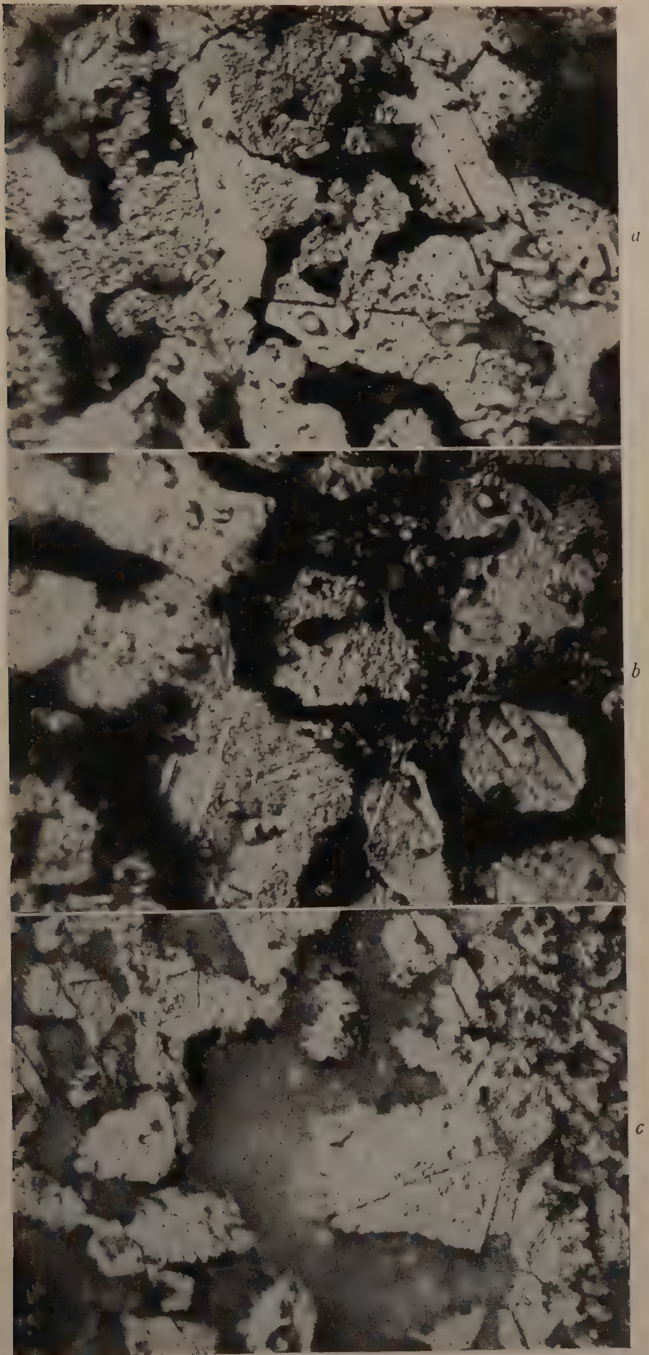

FIG. 12.—TWINS OF FORMER ALPHA IN COPPER PLUGS.
a. Pipe 200D, × 1400.
b. Pipe 134B, × 1400.
c. Pipe 31, × 750.

of beta is different from that of alpha in two respects: (1) beta is always attacked first, (2) dezincification of beta is often gradual, while that of alpha is always abrupt.

In many pipes the first sign of dezincification was change in the color of beta, which turned black. In these pipes there were three kinds of "beta" patches near the plugs: (1) completely filled with copper, (2) black patches and (3) normal golden yellow (Pipe 16, Fig. 13*a*).

Microscopic study of dezincification of beta at high magnifications revealed that in theinitial stage only slight roughening of the beta surface occurred (Fig. 13*b*). This change is responsible for the discoloration of beta, apparent at lower magnifications. The real structure remained unresolved. In the final stage of dezincification the view cleared up, and the copper was distinctly seen completely filling the space of the former patches of beta. It contained many black and reddish brown lines and dots (Fig. 13*c*).

The latter were first interpreted as a structural constituent but after repeated examinations the reddish specks were found to be pits in the copper with bright walls, which reflected the natural color of this metal. It became evident that the porous copper was the only product of dezincification in its final stage, as far as the microscope could reveal. All further efforts to determine the structure of the copper have failed. Judging from the fact that completely corroded patches of "beta" were maintaining their shape for a long time, until an increased porosity and the ultimate oxidation of copper had destroyed all vestiges of the original structure, the authors are inclined to believe in the residual origin of the copper formed by dezincification of beta. The preservation of shape indicates that the process did not entirely ruin the skeletons of beta that continued to exist.

It would be erroneous to say, however, that precipitation of copper does not occur in the corrosion of brass pipes. Evidence of such precipitation was found by the authors in one of the tubercles where small deposits of copper were disclosed among other minerals, but this copper had been carried by the corrosive water from somewhere else and not deposited in situ.

PERIODICITY OF CORROSION

Periodicity of corrosion processes has been mentioned in the literature by one of the authors[20] who observed in the patina of ancient bronzes parallel bands of cuprite and malachite arranged in alternating order (Fig. 14*a*). These minerals are common products of corrosion of old bronzes. In some specimens the number of bands exceeded 50 and their average width was from 4 to 5 microns. The formation of these bands in bronze patina could be explained only by a certain periodicity of the corrosion process. At first it was attributed to seasonal changes in the burial ground, but when further examinations revealed similar periodicity within individual grains of bronze that were partially or totally corroded, the periodicity appeared closely associated with the mechanism of corrosion within the crystals (Fig. 14*b*). These grains contained concentric zones of two different mineral products arranged alternately. It seemed as though the corrosion of each grain had been going on with a periodical rise and drop of concentration of the corrosive liquid, or passing through a cycle of some intermittent chemical or electrochemical changes.

Periodic type of corrosion was found in ancient copper and silver also. During the present examination of brass pipes it was first encountered in plugs and tubercles. The structure of plugs consisted of many concentric zones distinctly visible in their vertical and horizontal sections (Fig. 7). As has already been explained,

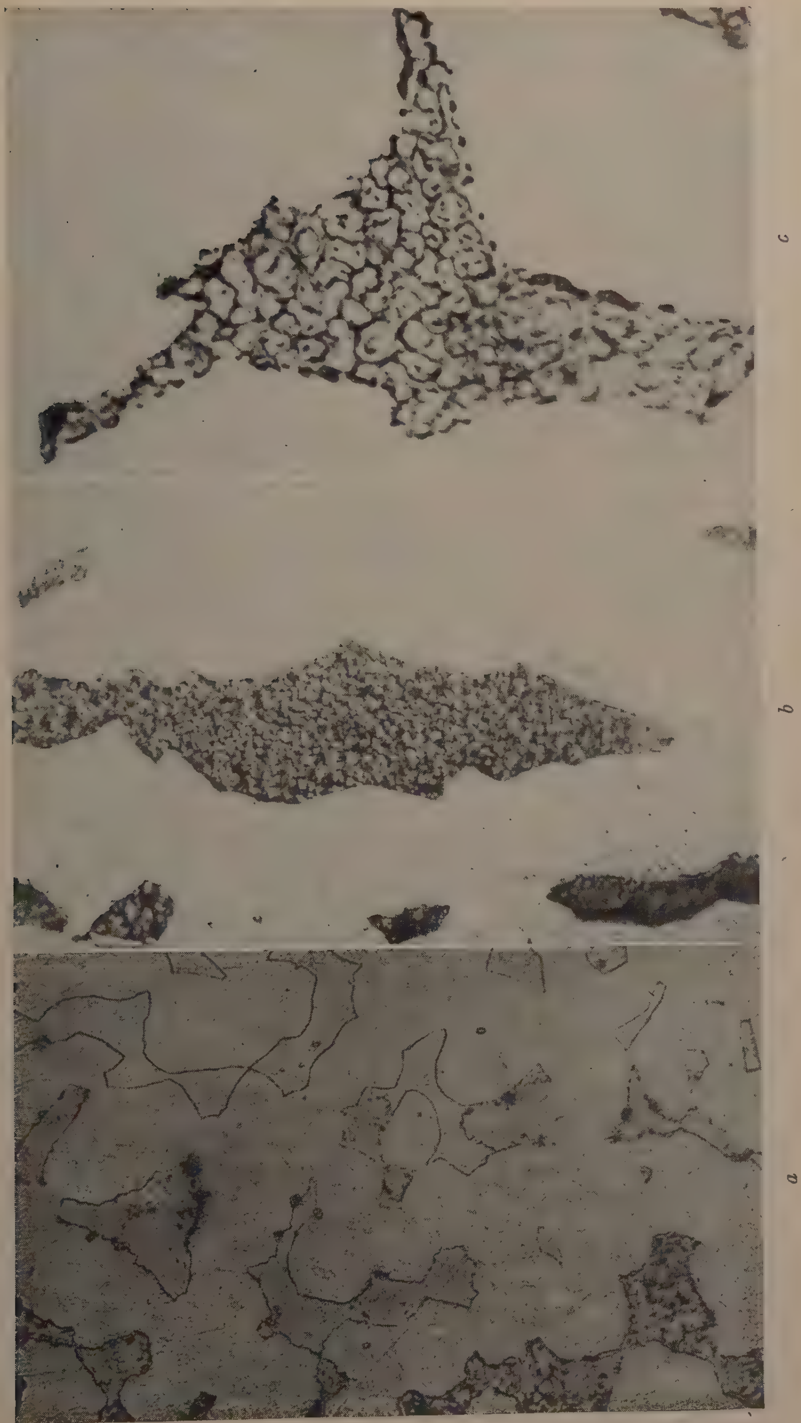

FIG. 13.—DEZINCIFICATION OF BETA.
a. Gradual dezincification, pipe 73. × 400.
b. Roughening of surface in initial stage, pipe 125. × 1500.
c. Final stage, pipe 54. × 2000.

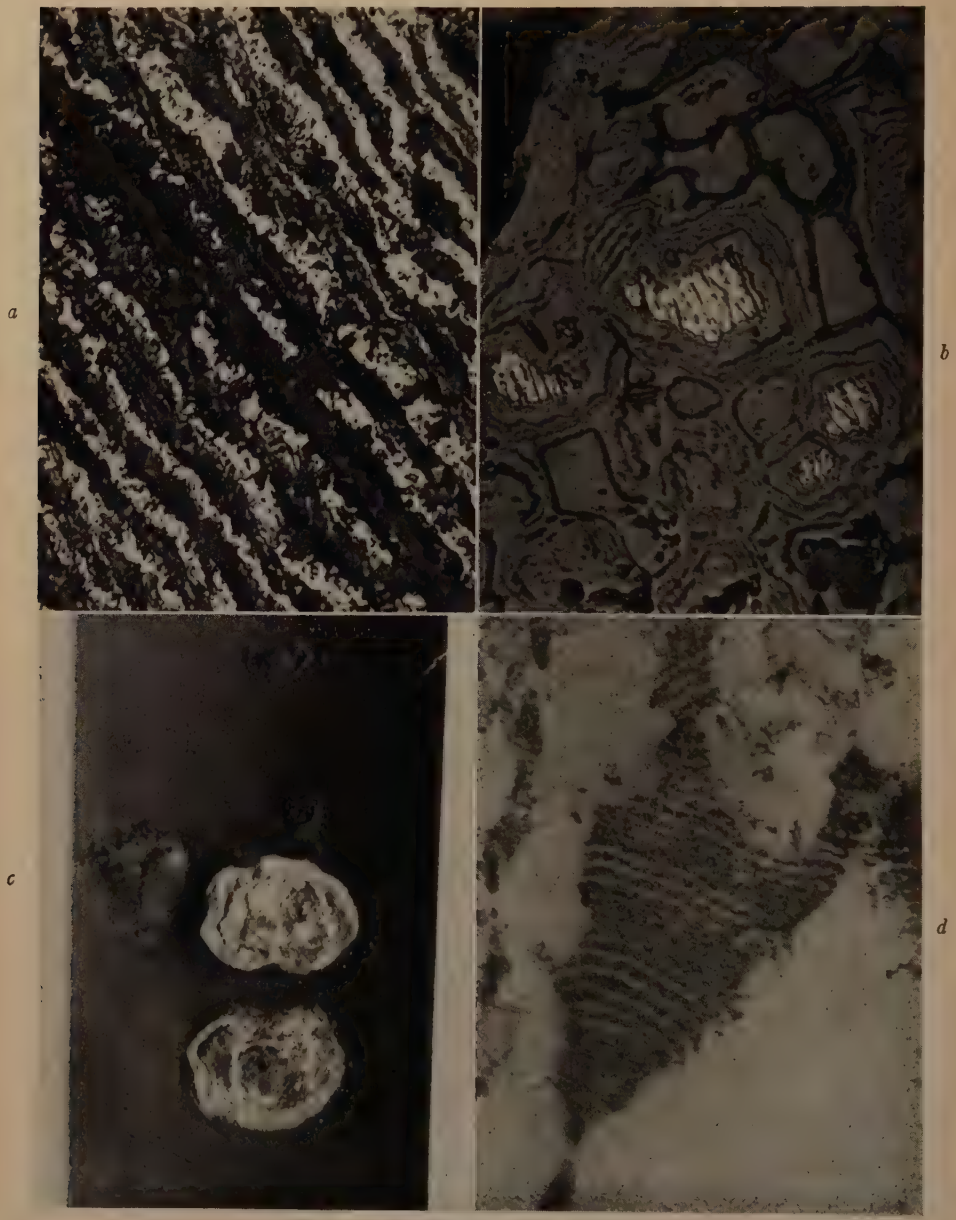

FIG. 14.—PERIODICITY OF CORROSION.
a. Parallel bands of cuprite and malachite in ancient bronze. × 100.
b. Zonal structure of corroded grains in ancient bronze. × 1000.
c. Fracture of tubercle, showing concentric shells. × 3.
d. Alternating bands of Cu_2O and copper in corroded beta, pipe 125. × 1000.

the main difference between the zones was in the amount of porosity, the dark zones being more porous than the light ones. Periodicity of a tubercle's formative process was evident from the presence of many concentric shells in the walls of tubercles (Fig. 14*c*). Often the shells were separated by spaces.

A different type of periodicity was revealed in pipe 125, where some patches of corroded beta showed numerous stripes (Fig. 14*d*). At high magnifications they appeared to be bands of metallic copper alternating with bands of cuprous oxide. The total number of these bands in one patch of beta was 60 on a length of 75 microns, the average width of each being slightly over one micron. We can only speculate as to the reasons why the beta in this particular location was not converted into solid copper or solid cuprous oxide as it was in all other corroded parts of the same pipe.

In conclusion, it should be noted that inasmuch as corrosion causes structural changes, the current theories of corrosion should take these changes into consideration.

SUMMARY

The corrosion of yellow brass pipes removed from domestic hot-water installations was studied under the microscope in relation to their microstructure and conditions of service. Particular attention was given to the study of the structural aspects of corrosion, the origin of local corrosion, the nature of copper deposits, and general conditions of dezincification. The results are briefly outlined below:

1. All pipes were found corroded, but the rate of general corrosion per year was small, and some specimens were in good condition after 20 to 25 years of service. However, most of the pipes exhibited local corrosion, which was much more destructive.

2. The size of grains apparently had no effect on corrosion, except perhaps when it varied considerably; but the surface defects of pipes, the residual straining of metal and cracks were influential factors.

3. Corrosion of both constituents of brass, alpha and beta, had two distinct stages, dezincification and the final corrosion of copper formed. The lag between these stages varied considerably.

4. In alpha-beta brass pipes, the beta was always attacked first, but here also the lag varied considerably.

5. Microscopic examination revealed that local corrosion in some pipes was closely associated with residual stresses and local deformations. The evidence thus obtained pointed to the conclusion that these factors were influential in starting the localized corrosion in these pipes.

6. Conclusive evidence of the residual origin of copper derived from dezincification of alpha was found in the structural characteristics of the deposits. In regard to the copper derived from dezincification of beta, the residual origin is the most probable.

7. The presence of alternating zones in plugs and also the zonal structure of tubercles indicated that some periodic changes were involved in the process of corrosion. Further evidence of periodicity was found in corroded "beta," which displayed parallel bands of copper and cuprous oxide arranged in alternate order. Periodicity of corrosion observed in other metals is mentioned.

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DISCUSSION

W. M. BALDWIN, JR.*—In reviewing the summary of this paper, the writer would like to suggest some caution with regard to the sixth point. The "conclusive evidence of the residual origin of copper" is based on the authors' reasoning that, "it seemed certain that if the zinc had been selectively leached out, some of the aspects of the original metal should still be found; . . . on the other hand, assuming that copper had been redeposited, the microstructure of the deposits should necessarily be typical of metals precipitated from aqueous solutions." It is rather difficult, of course, to define just what the *typical* microstructure of metals precipitated from aqueous solutions is. A multitude of factors can influence the manner in which precipitates are deposited. Maddigan,[22] in reviewing Smith's studies of the precipitation of iron in brass, has outlined some interesting facts regarding precipitation, which can bear repeating here.

"Bunn[23] and other workers," he writes, "have shown that in precipitation of certain salt crystals from solution the crystal habit of growth may be entirely changed by small additions of a second salt which is coprecipitated as a mixed crystal. Furthermore, definite orientation relations exist when one of these salts is precipitated as an overgrowth upon a crystal of the other. It has further been found that certain insoluble salts can precipitate some others as overgrowths from *unsaturated* solutions, provided the two salts have similar lattices with atom separations differing by less than about 10 percent.[24]"

Savage[25] writes, "it is possible under carefully controlled conditions to electrodeposit one metal upon another and maintain the same crystal orientation in the deposit as that of the basis metal. At times the grains in the deposit are a continuation of the grains in the surface of the basis metal." Savage based these remarks undoubtedly on the reported experimental work of Wood,[26] Cochrane,[27] Thompson,[28] Huntington,[29] Graham,[30] Hothersall,[31] Blum and Rawdon,[32] Tammann and Straumanis et al.[33] Barrett,[34] on reviewing Hothersall's work, writes, "When both metals are cubic, continuation is found only if the base metal has a parameter approximately equal to that of the deposit (2.4 per cent smaller to 12.5 per cent greater)." It might be stated parenthetically at this point that both alpha brass and copper are face-centered cubic, the former having a lattice parameter (at 35 per cent Zn) of 3.689+, while for the latter $a = 3.609+$, so that the parameter of brass in this instance would be about 2.5 per cent greater than copper.

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* Chase Brass and Copper Co., Cleveland, Ohio.

[22] References are on page 231.

It is not the intent of the writer to give the impression by selected references that the *typical* mode of deposition is necessarily that in which the film assumes the same or a related orientation as the basis metal; it is his intent to show merely that such cases do exist and are not uncommon.

This evidence indicates that the possibility exists that copper *could* be redeposited against alpha brass, assuming the crystal structure and appearance of the brass itself, hence the appearance of twinned grains of copper in a dezincified plug do not offer conclusive evidence of leaching: they merely constitute an interesting phenomenon that could occur whether the plug was formed by deposition of copper or by selective leaching of zinc.

E. P. POLUSHKIN (author's reply).—Our statement about the residual origin of copper deposits in dezincified alpha brass was based on direct observation. We found that some of the corroded alpha grains still retain their shape and show the original twinning, although their color has changed to red. The preservation of the original structural pattern points to a leaching process rather than to redeposition of copper from a solution Crystals deposited from liquid solutions usually assume a regular polyhedral or dendritic shape (if the crystallization process was not completed), or, in case of deposition from an electrolytic bath, form aggregates of closely piled crystals. In polished or etched sections the electrolytic deposits invariably show banding. None of these characteristics were found in the copper deposits of corroded brass. If we assume that copper was deposited on alpha, then, in some crystals of alpha in which corrosion only partially destroyed the original pattern of alpha, the interface should show a distinct line of demarkation between the old and new structures. This was not in evidence, however. Instead, we observed occasionally skeletons of typical twinned alpha grains with their yellow color changed to red. In salt crystals the mode of deposition may be entirely different.

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The Alpha Solid Solution Field of the Copper-manganese-zinc System

By R. S. Dean,* Member, J. R. Long,† Member, T. R. Graham,† Junior Member A.I.M.E., and A. H. Roberson‡

(New York Meeting, February 1945)

Experimental work on the properties of high-purity alloys of the copper-manganese-zinc system has necessarily required extensive metallographic work to determine the equilibrium conditions in this system. Previous work on these alloys is fragmentary and, unfortunately, based on alloys made with impure grades of manganese, thus introducing significant amounts of iron, silicon, aluminum and carbon. Since these elements are known to affect equilibrium conditions, it became desirable to re-examine these alloys made from the pure metals. The alpha solid solution field was of particular interest and, therefore, was chosen for the initial work, which was outlined to determine the composition limits of this field.

Previous Work

Heusler[1] conducted an extensive survey of the liquid-solid regions of this system and also made an estimate of the solid-phase boundaries at 340°C. The pertinent part of his diagram is given in Fig. 1, but it is of limited usefulness, since it applied to a single temperature only and is based on impure alloys under admittedly nonequilibrium conditions. Bauer and Hansen,[2] likewise working with impure alloys, have determined the phase boundaries for alpha-beta brasses containing small amounts of manganese and indicate an increase in the extent of the alpha field with increasing manganese. This is not in accordance with Heusler or with data obtained on pure alloys.[3] They also described a third constituent precipitating in the alpha plus beta field below 350° to 400°C. but did not identify this constituent. Guillet[4] and Heike and Ledibur[5] have also noted this precipitate.

Each of these investigators recognized that impurities present in the manganese could and did have an effect on the structure and properties of their alloys. Corson[6] in particular pointed out the hardening effects of silicon, aluminum, and carbon in copper-manganese alloys and Heusler reported that his alloys containing more than 25 per cent manganese were extremely brittle. In all probability this brittleness was due to the impurities present. This early work, therefore, should be taken as a general guide for preliminary studies only, and high-purity alloys may be expected to produce different results. The work of the Bureau of Mines laboratories with electrolytic manganese has been briefly summarized by Dean[7] but includes only a short section on this system. Later work[3] outlined a limited portion of the alpha field in the neighborhood of 65 per cent copper, 10 per cent manganese, and 25 per cent zinc. The present work was under-

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[1] References are at the end of the paper.

taken to define the field more completely and to note the changes that occurred with temperature.

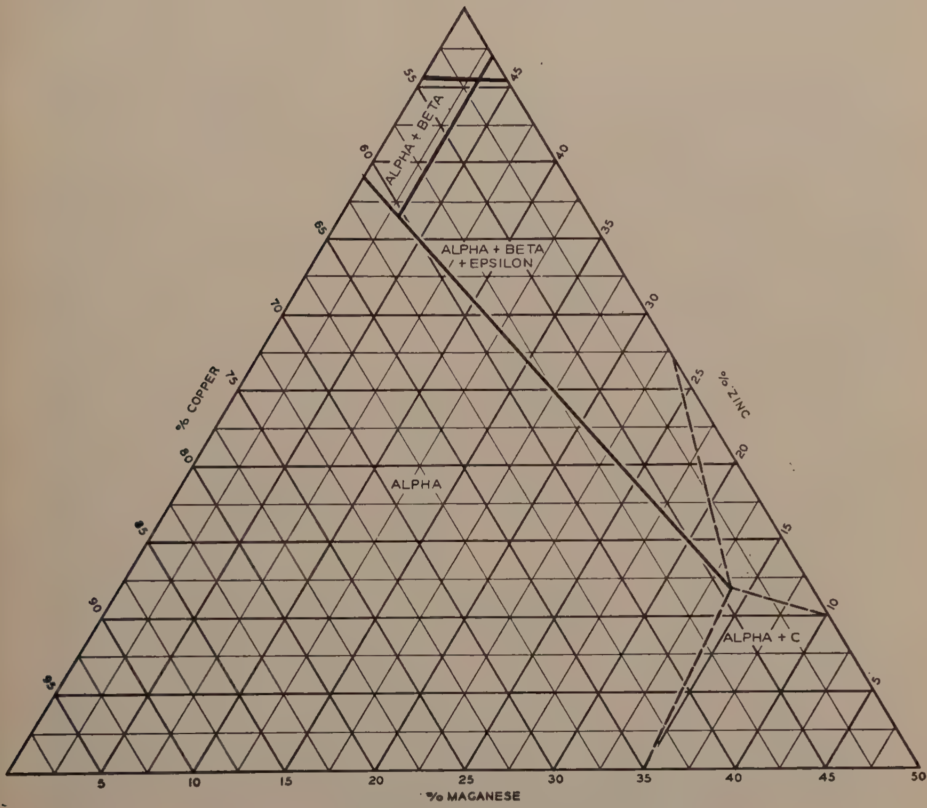

FIG. 1.—PART OF HEUSLER'S PHASE-BOUNDARY DIAGRAM.

TABLE 1.—*Chemical Analysis of Metals Used*

PER CENT

Copper		Manganese		Zinc	
Fe......	0.008	Fe.........	0.01	Fe.......	<0.01
S.......	<0.01	S..........	0.02	S........	<0.01
Ni......	<0.01	Si.........	nil	Pb......	<0.01
As, Sb, Sn, Pb.....	nil	Al.........	nil	Cd......	<0.01
		Pb.......	0.02	As, Sb, Sn	nil

EXPERIMENTAL WORK

The alloys used were prepared from electrolytic manganese, wirebar-grade copper, and high-purity zinc. Typical analyses for these materials are given in Table 1. These do not represent adequately the purity of the zinc, since this material is actually of the 99.99+ per cent grade. The values given were obtained in routine chemical analyses and as they were satisfactory for our work further analyses by spectroscopic methods were deemed unnecessary. The purity of the manganese is worthy of note, since this metal introduced most of the impurities that occurred in the alloys previously used. Melting practice generally consisted of melting the copper in a high-frequency furnace, adding the manganese and then the zinc. Small amounts of aluminum were added for deoxidation just prior to pouring. Such additions were carefully regulated to avoid excessive residual aluminum, since it has been found to have considerable effect on the structures of the alloy. The residual

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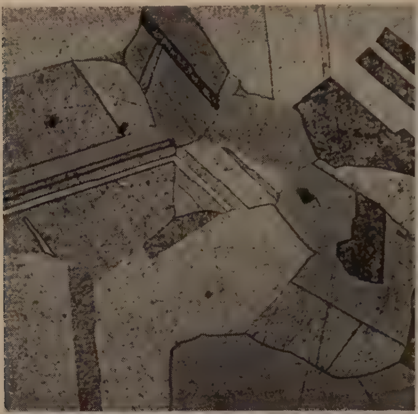

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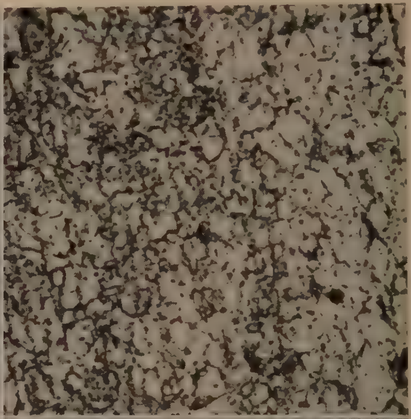

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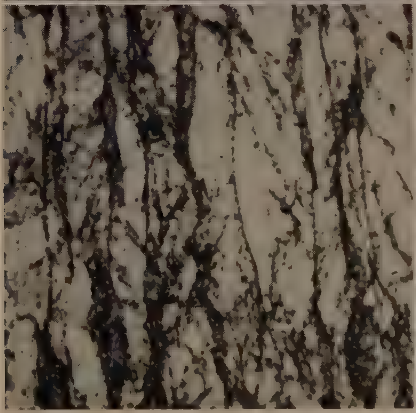

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FIG. 2.—ALPHA SOLID SOLUTION. × 100.
65.5 per cent Cu, 19.9 per cent Mn, 14.8 per cent Zn. Quenched from 1500°F.
FIG. 3.—ALPHA PLUS *X*. × 250.
62.5 per cent Cu, 19.7 per cent Mn, 17.7 per cent Zn. After 200 hours at 800°F.
FIG. 4.—ALPHA + *X*. × 500.
55.0 per cent Cu, 24.8 per cent Mn, 20.4 per cent Zn. Heated 1 hour at 900°F.
FIG. 5.—ALPHA + *X* FROM BETA. × 250.
52.5 per cent Cu, 24.6 per cent Mn, 23.0 per cent Zn. Soaked 24 hours at 800°F.

aluminum exceeds 0.05 per cent in only a few instances (Table 2). These were made for other purposes and had larger amounts of aluminum intentionally added. They are included to show the trend of the alpha plus *X* boundary at 1100°F. only.

The chill-cast slab ingots were hot-rolled and then cold-rolled with intermediate annealing to produce 0.0625-in. sheet finished with 60 per cent cold reduction. Cold-worked material was used as the starting point because past experience with similar alloys indicated that equilibrium could be approached more readily by heat-treatment of cold-worked material. Pieces of the alloys were heated to temperatures ranging from 800° to 1500°F. for time periods depending on the temperature range. They were water-quenched from the soaking temperature.

The phases present in each alloy after quenching from the various temperatures were determined microscopically and the identity of the constituents observed was confirmed by X-ray diffraction patterns made on representative structures. The specimens were held at temperature ½, 1, 4, 24 and 48 hr. for temperatures from 800° to 1000°F. (426° to 538°C.) and ½, 1, and 4 hr. at temperatures from 1100° to 1500°F. (593° to 815°C.). Some differences in structures were observed between specimens of the same alloy held for less than 24 hr. at temperatures of 1000°F. and below, but none between those held 24 and 48 hr. These differences were chiefly in the amount of the phases present and did not alter the position of the phase boundaries significantly. Since the specimens held for 24 and 48 hr. showed the same structures, it is believed that phase boundaries based on 48 hr. soaking time for temperatures up to 1000°F. are representative of equilibrium conditions. Likewise, specimens held for 1 and 4 hr. at 1100° to 1500°F. had

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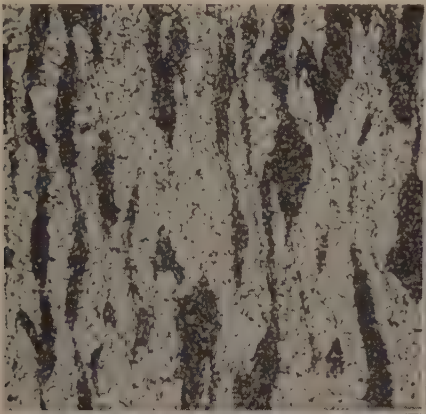

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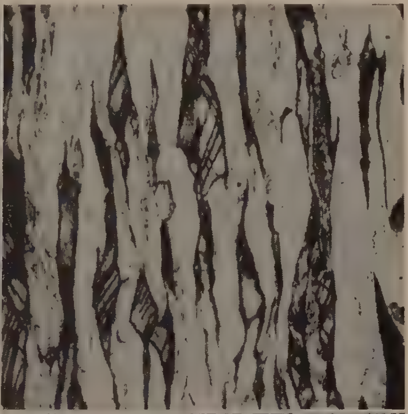

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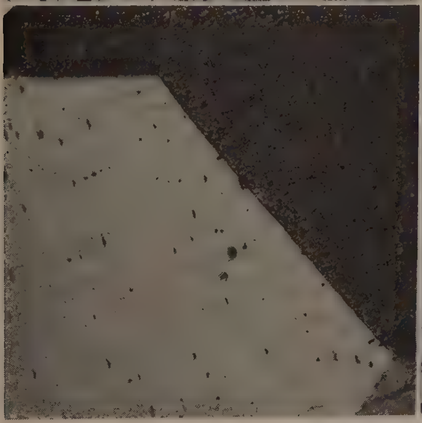

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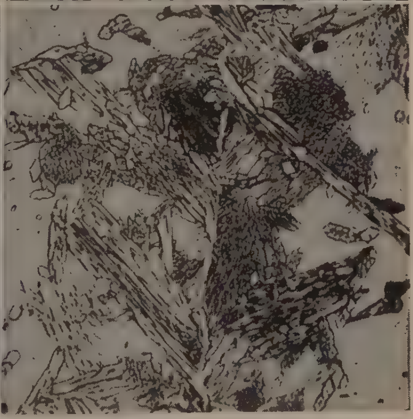

FIG. 6.—ALPHA + X FROM ALPHA PLUS BETA.

57.6 per cent Cu, 19.7 per cent Mn, 22.2 per cent Zn. Segregation of X from beta after 200 hours at 800°F.

FIG. 7.—ALPHA + BETA.

57.6 per cent Cu, 19.7 per cent Mn, 22.2 per cent Zn. Cold-worked structure.

FIG. 8.—BETA SOLID SOLUTION.

52.5 per cent Cu, 24.6 per cent Mn, 23.0 per cent Zn. Quenched from 1500°F.

FIG. 9.—BETA WITH FRINGE OF ALPHA NEEDLES.

60.2 per cent Cu, 19.5 per cent Mn, 20.5 per cent Zn. Quenched from 1500°F.

All × 250.

essentially the same structures and differed but slightly from those obtained after ½ hr. at temperature. It is believed therefore that the data for 4 hr. at these temperatures also represents a reasonable approach to equilibrium as far as the phases present are concerned. True equilibrium, however, is not necessary to establish the limit of a single-phase field if some precipitation occurs in those alloys that fall outside of the field; that is, the presence of the second phase is all that is necessary to establish the limits of the field. Whether or not the second phase is present in equilibrium amounts is not important. The fact that all of these alloys were heat-treated from the cold-worked condition contributed to their rapid response to heat-treatment. Microscopic examination was found to be much more sensitive than hardness, conductivity, dilatometry, or X-ray examination for detecting the presence or absence of a second phase in these alloys and accordingly the phase boundaries established are based primarily on the structures observed as given in Table 2.

MICROSTRUCTURE

In the range of compositions examined, the microconstituents of the alloys were: (1) alpha, the copper-rich, simple face-centered cubic solid solution: (2) beta, the complex body-centered cubic solid solution of the brasses; and (3) an unidentified constituent designated as *X* (no doubt Heusler's *C* phase). This constituent was thought at first to be alpha manganese because of its resemblance to the precipi-

TABLE 2.—*Microstructure of Alloys along Alpha Solubility Line* Cu-Mn-Zn *Ternary Diagram*

Alloy No.	Analysis, Per Cent						Microstructure[a]							
	Cu	Mn	Zn	Al	Fe	Si	1500°F. 4 hr.	1400°F. 4 hr.	1300°F. 4 hr.	1200°F. 4 hr.	1100°F. 4 hr.	1000°F. 48 hr.	900°F. 48 hr.	800°F. 48 hr.
1	74.9	15.5	9.8	0.05	0.016	Nil	A	A	A	A	A	A	A	A
2	74.5	19.8	5.1	0.13	0.017	Nil	A	A	A	A	A	A	A	A
3	69.4	15.9	14.5	0.05	0.021	Nil	A	A	A	A	A	A	A	A
4	70.0	20.4	9.3	0.04	0.019	Nil	A	A	A	A	A	A	A	A
5	70.3	24.5	4.8	0.04	0.017	Nil	A	A	A	A	A	A	A	AX
6	67.9	5.3	27.0	0.02	0.005	Nil	A	A	A	A	A	A	A	A
7	68.1	14.4	17.3	0.02	0.005	Nil	A	A	A	A	A	A	A	A
8	64.4	5.1	30.2	0.06	0.008	Nil	AB	AB	A	A	A	A	A	A
9	64.8	9.95	25.4	Nil	Nil	Nil	AB	A	A	A	A	A	A	A
10	65.0	14.7	20.3	0.02	0.005	Nil	AB	A	A	A	A	A	A	A
11	65.5	19.9	14.8	0.02	0.005	Nil	A	A	A	A	A	A	A	AX
12	64.7	25.6	9.4	0.04	0.029	Nil	A	A	A	A	A	A	AX	AX
13	62.6	5.1	32.0	0.02	0.008	Nil	AB	AB	AB	AB	AB	A	A	A
14	62.3	10.0	27.2	0.02	0.005	Nil	AB	AB	AB	A	A	A	A	A
15	63.0	14.5	22.3	0.02	0.005	Nil	AB	AB	A	A	A	A	A	AX
16	62.5	19.7	17.7	0.02	0.005	Nil	AB	A	A	A	A	A	A	AX
17	60.1	5.0	35.1	0.04	0.008	Nil	B	B	AB	AB	AB	AB	AB	AB
18	60.5	9.8	29.8	0.02	0.005	Nil	B	AB	AB	AB	AB	AB	A	AX
19	60.5	14.6	25.0	0.02	0.005	Nil	B	AB	AB	AB	A	A	A	AX
20	60.2	19.5	20.5	0.02	0.005	Nil	AB	AB	A	A	A	A	A	AX
21	59.7	24.8	15.0	0.02	0.005	Nil	AB	AB	A	A	A	A	AX	AX
22	57.6	19.7	22.2	0.02	0.005	Nil	B	B	AB	AB	AB	A	AX	AX
23	57.5	24.6	17.8	0.02	0.005	Nil	B	AB	A	A	A	AX	AX	AX
24	56.5	30.7	12.9	0.08	0.026	Nil	AB	A	A	A	A	AX	AX	AX
25	55.0	24.8	20.4	0.02	0.005	Nil	B	B	AB	AB	AB	AX	AX	AX
26[b]	55.0	29.6	14.4	0.41	0.07	Nil	AB	AB	A	A	A	AX	AX	AX
27[b]	55.2	34.1	11.2	0.29	0.09	Nil	AB	A	A	A	AX	AX	AX	AX
28	52.5	24.6	23.0	0.02	0.005	Nil	B	B	B	AB	AB	ABX	AX	AX
29	53.1	29.5	17.5	0.05	0.005	Nil	B	B	A	A	A	AX	AX	AX
30	52.5	34.6	12.7	0.05	0.005	Nil	AB	A	A	A	A	AX	AX	AX
31[b]	50.4	29.7	19.0	0.37	0.08	Nil	B	B	B	B	AB	AX	AX	AX
32[b]	50.2	34.4	14.2	0.23	0.11	Nil	B	AB	A	A	A	AX	AX	AX
33[b]	50.5	37.8	12.8	0.34	0.12	Nil	AB	A	A	A	AX	AX	AX	AX
34	48.5	33.8	17.6	0.02	0.005	Nil	B	B	B	AB	A	AX	AX	AX
35[b]	45.4	35.1	19.2	0.47	0.05	Nil	B	B	B	B	A	AX	AX	AX
36[b]	45.4	39.6	14.8	0.36	0.06	Nil	B	B	AB	A	AX	AX	AX	AX

[a] A = alpha; B, beta; X, face-centered cubic phase not yet identified.
[b] High residual aluminum alloys.

tate that occurs in copper-manganese alloys under certain conditions. Its X-ray diffraction pattern, however, is entirely different and has been tentatively classed as a face-centered cube with a rather large parameter. None of the alloys contained enough of the phase to permit an estimation of its chemical composition. It will be studied however, further to determine its constitution and position in the diagram. The most frequently encountered structures were alpha, alpha plus *X* and alpha plus beta. Only a few of the alloys fell in the beta field and these did not always show the usual beta structure as will be noted later.

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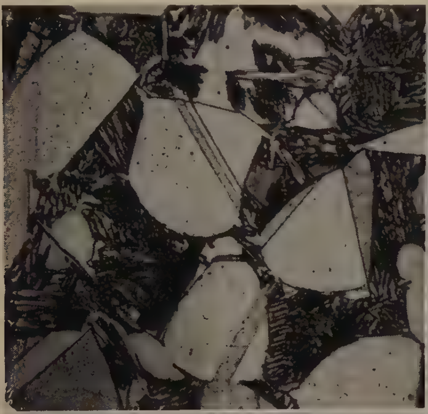

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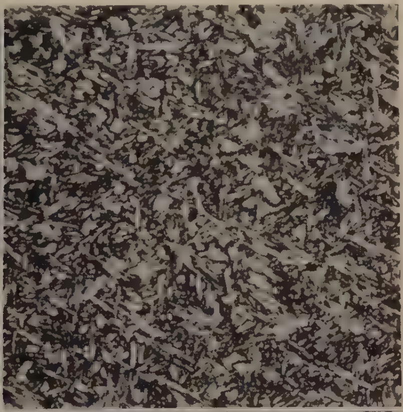

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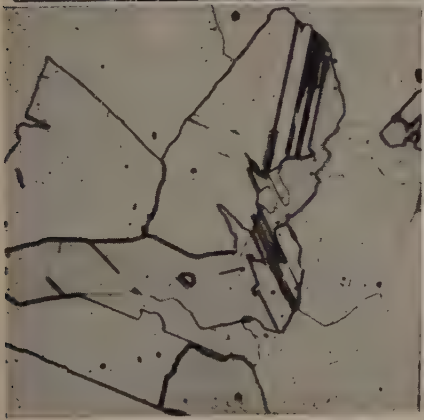

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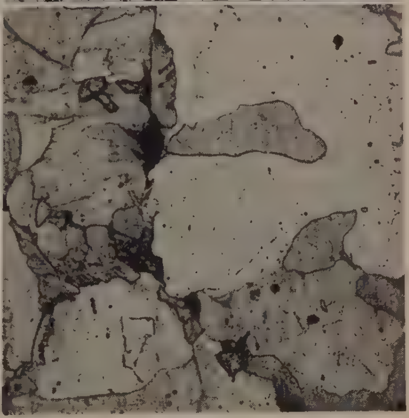

Fig. 10.—Alpha plus alpha needles from transformed beta.
62.6 per cent Cu, 5.1 per cent Mn, 32.0 per cent Zn. Quenched from 1500°F.
Fig. 11.—Alpha needles from transformed beta.
60.1 per cent Cu, 5.0 per cent Mn, 35.1 per cent Zn. Quenched from 1500°F.
Fig. 12.—Twinned alpha from massive transformation of beta.
53.1 per cent Cu, 29.5 per cent Mn, 17.5 per cent Zn. Quenched after 4 hours at 1500°F.
Fig. 13.—Alpha from massive transformation of beta. Twinning not obvious.
57.6 per cent Cu, 19.7 per cent Mn, 23.2 per cent Zn. Quenched after 1 hour at 1400°F.
All × 250.

The alpha solution as shown in Fig. 2 is typical of the single-phase copper alloys. The phase *X* precipitated from the recrystallized alpha can be seen in Fig. 3. When the treatment temperature was below the recrystallization range the *X*

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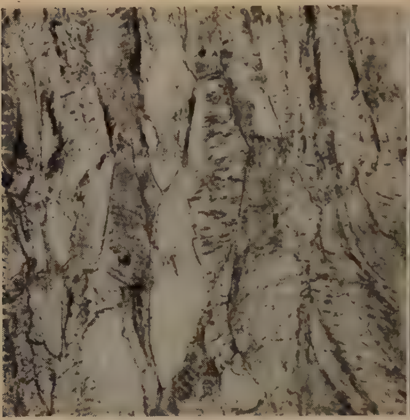

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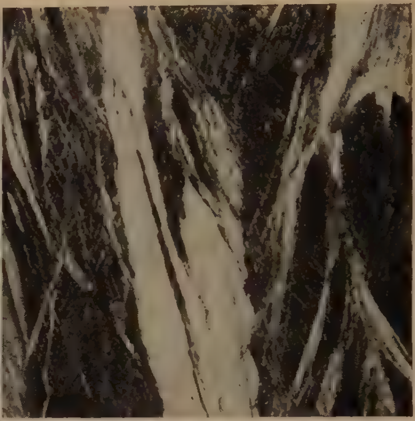

FIG. 14.—COLD-WORKED ALPHA SOLID SOLUTION.
67.9 per cent Cu, 5.3 per cent Mn, 27.0 per cent Zn.
FIG. 15.—COLD-WORKED BETA SOLID SOLUTION.
52.5 per cent Cu, 24.6 per cent Mn, 23.0 per cent Zn.
Both × 100.

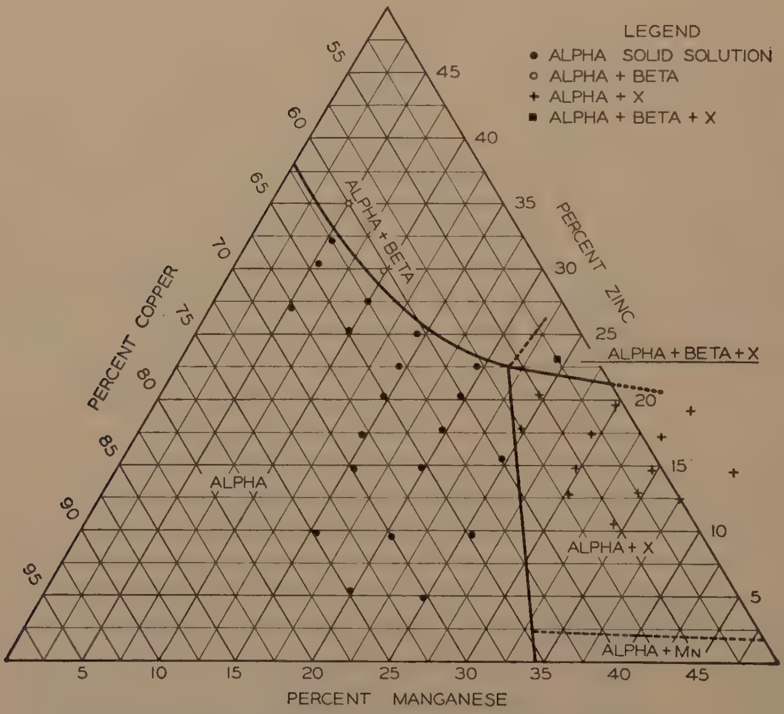

FIG. 16.—PHASE BOUNDARIES AT 1000°F. (538°C.).
Specimens held at temperature 48 hours and water-quenched.

formed in the cold-worked grain boundaries and slip planes as noted in Fig. 4. The appearance of *X* precipitated from the beta phase in Fig. 5, is remarkable because of the fine particle size and uniform distribution. Apparently the mechanism of precipitation from beta and from alpha differ markedly. Another interesting structure is found in Fig. 6. Here, the precipitation of the unknown is much heavier in some grains than in others. Prior to the cold-working this particular alloy had been heated in the alpha plus beta zone and upon reheating at 800°F. in the alpha plus *X* zone, precipitated more *X* from the areas that had been beta than from the ground mass of alpha. The relationship between the dense precipitates of this phase and the original beta grains is quite evident from Fig. 7, which shows the structure of this alloy before heat-treatment. This suggests that the composition of beta differs markedly from that of alpha and that it is probably much richer in zinc and manganese than the alpha.

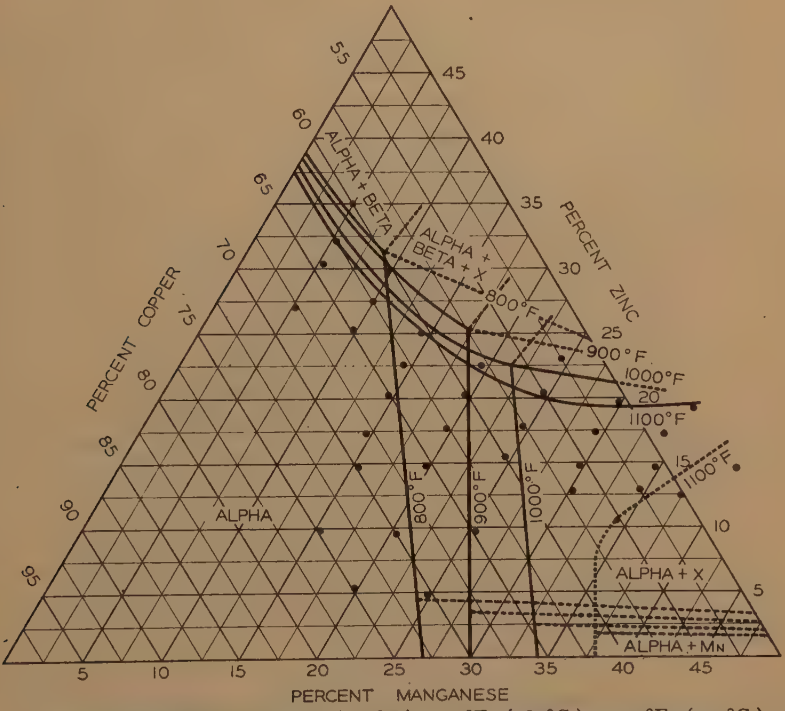

FIG. 17.—PHASE BOUNDARIES AT 800°F. (426°C.), 900°F. (482°C.), 1000°F. (532°C.), 1100°F. (593°C.).

Specimens for 800°, 900° and 1000°F. held at temperature for 48 hours and water-quenched. Specimens for 1100°F. held at temperature for 4 hours and water-quenched.

The typical beta solution structure is given in Fig. 8. This structure can be retained by quenching in some areas but in others it transforms quite rapidly and it is sometimes difficult to be certain of the structure that is stable at the quenching temperature. Beta grains with small needles of alpha from transformed beta in the boundary can be seen in Fig. 9. A similar structure obtained by quenching an alloy of slightly different composition from the alpha plus beta region is shown in Fig. 10. Another example of this rapid transformation is shown in Fig. 11. This alloy had been heated in the beta field and completely transformed during the quench, giving crisscrossing alpha needles. Small amounts of beta may be still present in this particular alloy.

When the transformation takes place with the formation of the alpha needles, the structure and its origin are not difficult to identify, but when it takes place by the conversion of whole grains of beta, bodily, into large alpha grains, it is often difficult to be sure of the structure under observation and the high-temperature structure from which it was formed. Such transformations occurring in brasses have been described and illustrated by Phillips.[8] Typical examples encountered in these alloys are shown in Figs. 12 and 13. These structures are essentially alpha solid solution formed by the transformation of beta during the quench, and their identity can be checked by the twinning and by X-ray diffraction patterns. The latter shows only the alpha solution to be present. This structure, however, is quite confusing when encountered in an unknown field and can easily be misinterpreted.

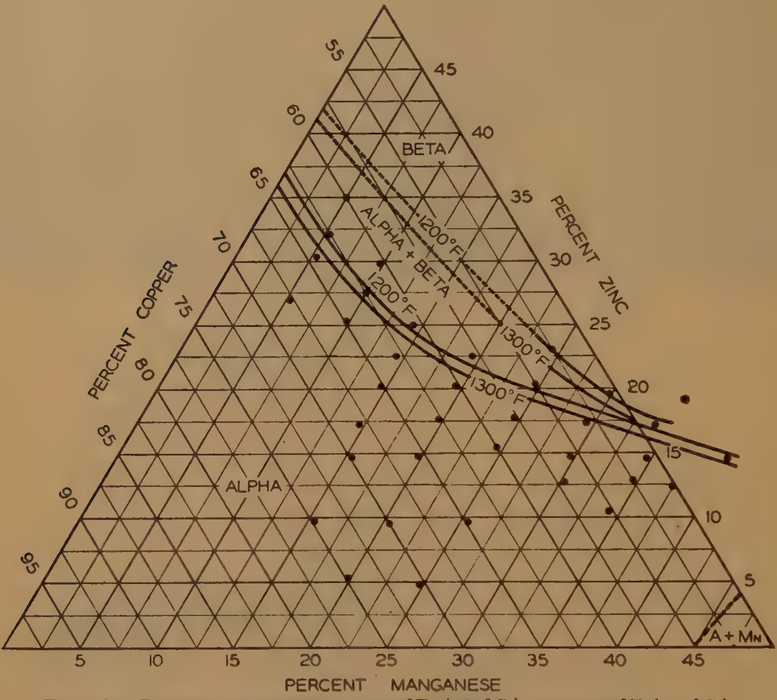

FIG. 18.—PHASE BOUNDARIES AT 1200°F. (684°C.) AND 1300°F (704°C.). Specimens held at temperature 4 hours and water-quenched.

Representative structures of the cold-worked condition are given in Fig. 14 for cold-worked alpha and Fig. 15 for cold-worked beta. The latter is worthy of note because this specimen had been cold-reduced 60 per cent. Alloys having higher zinc along with high manganese contents cannot be cold-worked nearly as much.

PHASE DIAGRAMS

Ternary plots of the phases found in the various alloys are given in Figs. 16 to 19, inclusive. These boundaries are drawn in accordance with the observed data and where possible, with due consideration to the relative amounts of the phases present. For purposes of general discussion the data for 1000°F. are plotted separately in Fig. 16. Here the alpha field is shown to be limited by the copper-zinc and copper-manganese binary systems on two sides and by the alpha plus beta and alpha plus *X* on the other two. The alpha plus *X* boundary is extended to the copper-manganese base line to correspond with the solubility of manganese in copper at the temperature involved[9] because the three fields, alpha, alpha plus *X*, and alpha plus manganese, must necessarily have a common meeting point. This extension is also justified by the alignment of the alloys showing the alpha and alpha plus *X* at temperatures of 800° and 900°F. The extension for 1000° and 1100°F. are not as well supported by the data but are so placed for the reason given. The alpha plus *X* field, however, must be separated from the base line by the alpha plus manganese field whose width at this point has not yet been established. Some fragmentary data on alloys other than those reported here indicate that it does not extend beyond the 5 per cent zinc line and such a boundary has been tentatively dotted in. Its course will be modified by the placement of the center of the *X* constituent and by additional investigation of alloys in the alpha plus manganese field.

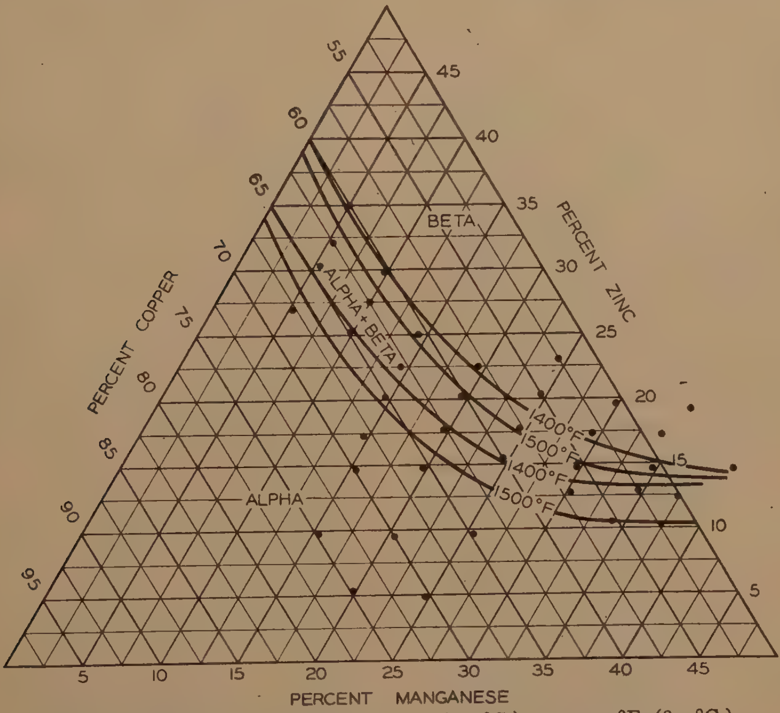

FIG. 19.—PHASE BOUNDARIES AT 1400°F. (760°C.) AND 1500°F. (815°C.). Specimens held at temperature 4 hours and water-quenched.

Heusler's diagram (Fig. 1) places a three-phase field adjacent to the alpha field but this is not a permissible construction. In the present study only one of the alloys examined gave any indications of three phases (alloy 28 at 1000°F.) and this was not conclusive. It should be noted here that the present alloys were chosen primarily to determine the outline of the alpha field only and determination of the extent and nature of adjacent fields must await the conclusion of other investigations now underway. If, however, an alpha plus beta plus *X* field exists, it would occur adjoining the alpha plus *X* and alpha plus beta fields, and would require that the extension of the alpha plus beta boundary, beyond the intersection with the alpha plus "X" boundary, be a straight line. This construction has been adopted since it provides for a three-phase field and is not inconsistent with the data at hand.

The intersection of the alpha-beta boundary with the copper-zinc base line has been placed in accordance with published data on that system.[10]

Initial additions of manganese to copper-zinc alloys have little effect on the alpha field, since the alpha-beta boundary parallels the lines of constant copper concentration up to 10 per cent manganese. At higher manganese content it curves through a broad arc to the intersection with the alpha plus *X* boundary. Beyond this, it is extended in a straight line as noted above.

At temperatures below 1000°F. the alpha field is restricted by precipitation of *X* with the alpha plus *X* boundary shifting to lower manganese contents in a roughly parallel fashion as shown in Fig. 17. Increasing temperatures widen the field by solution of *X* in alpha moving the alpha plus *X* boundary to higher manganese contents. Its position at 1100°F. is based on the high residual aluminum alloys previously mentioned and should therefore be taken as the upper limit of its position only. Aluminum in amounts of 0.3 to 0.5 per cent has been found to restrain precipitation of this phase and to decrease the reaction rates of the alloys. The line is dotted, to show its tentative nature. Beyond 1100°F. the alpha plus *X* boundary is outside the range of the alloys examined and in Fig. 18 it is based only on the solubility of manganese in copper and is therefore also dotted.

The alpha-beta boundary is affected but little by decreasing the temperature below 1000°F. but does show a definite tendency to move up toward higher zinc contents. Increasing temperature, however, produces considerable effects, shifting it to lower zinc contents especially at temperatures beyond 1200°F. This is in accord with the shape of this boundary in the copper-zinc binary system.

Some indication of the position of the beta boundary is given in Fig. 18 for temperatures of 1200° and 1300°F. and its course is definitely placed in Fig. 19 for 1400° and 1500°F. It is approximately parallel to the alpha-beta boundary indicating a considerable increase in the solubility of the beta solution for manganese at these temperatures.

The alpha field is considerably smaller at 800°F. (426°C.) than indicated by Heusler for 340°C. Since his alloys were heat-treated from the as-cast condition, probably they did not approach equilibrium in the 12-hr. soak given them. At this temperature they could be expected to be very slow to react. The impurities present would also introduce other variables. Comparison of Figs. 1 and 17 would suggest that his alloys more nearly corresponded to conditions stable at 1100°F. (593°C.).

SUMMARY

Using high-purity alloys, composition limits of the alpha field of the copper-manganese-zinc system have been determined for temperatures ranging from 800° to 1500°F. at intervals of 100°F. The field is bounded on two sides by the copper-zinc and copper-manganese binary systems, and by the alpha-beta and the alpha plus *X* fields on the other two sides. The alpha-beta boundary of the field remains approximately parallel to 60 per cent copper up to 10 per cent manganese and then curves toward the manganese corner with higher manganese contents. Increasing temperature moves the boundary toward the copper-manganese base line. The alpha plus X boundary at low temperatures is practically perpendicular to the copper-manganese base line and for 800°F. intersects the alpha-beta boundary at about 10 per cent manganese. With increasing temperature it is shifted to higher manganese contents in a parallel fashion, increasing the solubility of the alpha solid solution for manganese. Beyond 1100°F. this boundary appears to bend back toward the manganese corner.

Typical microstructures encountered have been described and illustrated. In particular, an unusual massive type of transformation of the beta solid solution to the alpha has been noted.

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A White High-manganese Brass

By R. S. Dean,* J. R. Long,† T. R. Graham,† Members A.I.M.E. and C. W. Matthews‡

(New York Meeting, February 1945)

In a previous paper§ the authors reported on the mechanical properties of a 65 per cent copper, 10 per cent manganese, 25 per cent zinc alloy as compared with similarly processed cartridge brass. Additional investigations by these laboratories, on higher copper alloys, have demonstrated that at lower zinc concentrations even larger amounts of pure manganese may be added to copper-zinc alloys without exceeding the single-phase solid solution limits, and that similar increases in tensile strength, yield strength, and hardness may be obtained without excessive decreases in ductility. Several compositions in this range showed also a decided color change with increasing manganese. The normal "brassy" color was considerably lightened and reduced to a faint yellow cast at 15 per cent manganese. With higher manganese contents the alloys were essentially white and similar in appearance to the nickel-silver alloys.

From this work it appeared that it would be desirable to determine more completely the properties of the wrought and annealed white alloys. Accordingly, a more detailed study was planned of an alloy having the composition 70 per cent copper, 20 per cent manganese, and 10 per cent zinc. This alloy remained single-phase throughout the working and annealing cycles of the preliminary tests and appeared to be about the strongest of the white single-phase alloys. The project included also an investigation of additional alloys, deviating from this composition by 5 per cent of each of the three components to evaluate the effects of variation in composition and a study of the properties of the central alloy made with silicothermic manganese.

Material Preparation

Electrolytic manganese, wirebar copper, and electrolytic zinc were used for the preparation of the alloys. Representative analysis of the electrolytic manganese seldom exceeds 0.01 per cent iron, 0.02 per cent sulphur and 0.02 per cent lead, with no silicon or aluminum. A typical sample of the silicothermic manganese metal contained 2 per cent iron, 0.81 per cent silicon, 0.16 per cent carbon, and 0.36 per cent aluminum. Melting and alloying were performed in a high-frequency furnace with magnesia crucibles. Melts were deoxidized with small aluminum additions and cast into 25-lb. slab ingots. Care was exercised in deoxidation to avoid excessive amounts of residual aluminum, which has been found to have significant effects on alloys in this system. All ingots were hot-rolled at 1200° to 1300°F. and then cold-rolled with intermediate anneal-

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§ J. R. Long and T. R. Graham: *Trans.* A.I.M.E. (1944) **156**, 222.

ing on a schedule calculated to produce sheet finished to 0.0625-in. thickness, with various amounts of cold-work. Preliminary testing of the central alloy showed that annealing for 1 hr. at 1200°F. after 60 per cent cold reduction, produced an average grain size of 0.065 mm., which was considered satisfactory for subsequent working and was adopted for the annealing cycles.

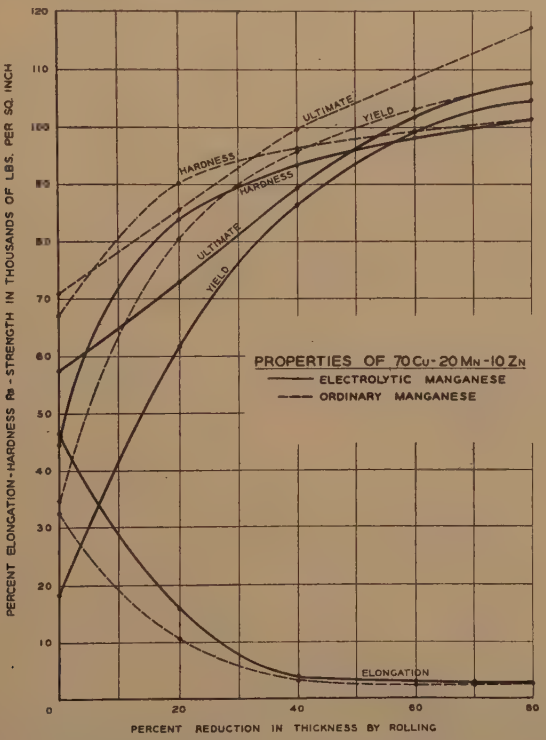


FIG. 1.—MECHANICAL PROPERTIES OF ELECTROLYTIC AND SILICOTHERMIC MANGANESE ALLOYS AS A FUNCTION OF COLD-WORK.

TABLE 1.—*Chemical Analysis*
PER CENT

Alloy No.	Cu	Mn	Zn	Al	Fe	Si
1	70.0	20.4	9.3	0.05	0.019	Nil
2	68.6	20.1	10.5	0.17	0.420	0.11
3	74.5	19.8	5.1	0.13	0.017	Nil
4	65.5	19.9	14.8	0.02	0.005	Nil
5	69.4	15.9	14.5	0.08	0.021	Nil
6	74.9	15.5	9.8	0.04	0.016	Nil
7	64.7	25.6	9.4	0.04	0.029	Nil
8	70.3	24.5	4.8	0.04	0.017	Nil

The microstructures of the alloys were examined prior to the final cold reduction, to check the grain size and cleanliness. All of the specimens were quite uniform, reasonably clean, free from nonmetallics, laminations, and other internal defects. The electrolytic manganese alloy had a ready-to-finish grain size of 0.065 mm., while the silicothermic manganese alloy consistently had an 0.010-mm. grain size. This small grain size is characteristic of alloys made with silicothermic manganese, and in subsequent annealing at higher temperatures it continued to show a much smaller grain size than the electrolytic manganese alloy at any given temperature.

MECHANICAL PROPERTIES

The tensile strength, yield strength, elongation, and hardness were determined on standard tensile specimens with a 2-in.

gauge length. The properties as cold-worked were obtained on material that had been reduced 0, 20, 40, 60, and 80 per cent in thickness by cold rolling after a 1-hr. anneal at 1200°F. The properties as annealed were determined on 60 per cent cold-reduced material heated for one hour at temperatures ranging from 400° to 1500°F. at intervals of 100°F. At least four specimens were tested in each condition and their properties were averaged for the tables and graphs. The data on the individual specimens were quite consistent, with little scatter beyond normal experimental error.

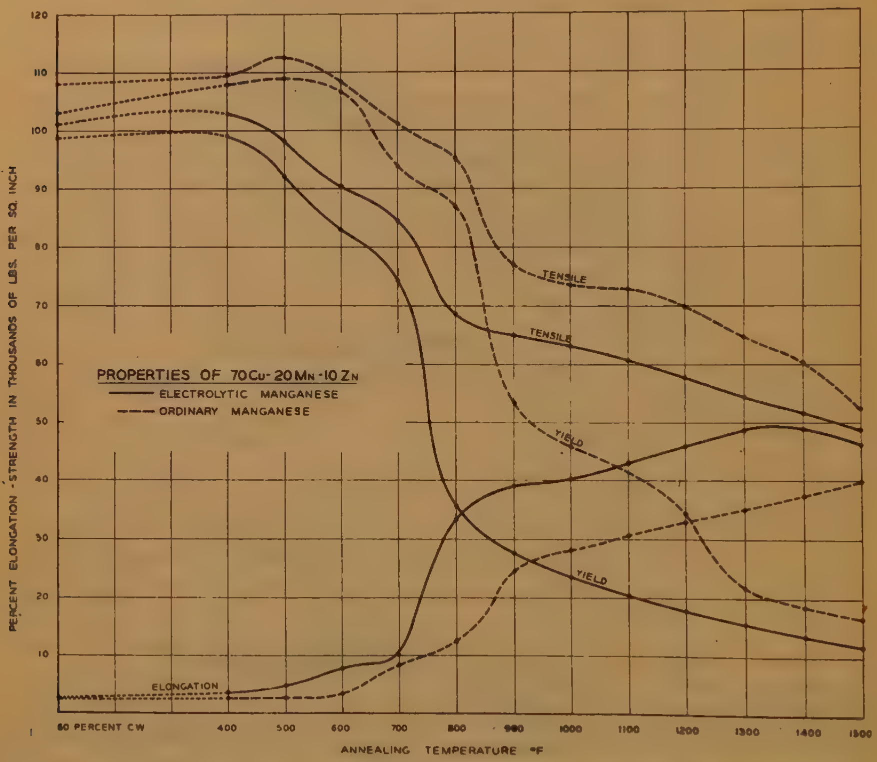


FIG. 2.—EFFECT OF ANNEALING TEMPERATURE ON TENSILE STRENGTH, YIELD STRENGTH, AND ELONGATION OF ELECTROLYTIC AND SILICOTHERMIC MANGANESE ALLOYS.

The properties of the 70 per cent copper, 20 per cent manganese, 10 per cent zinc alloy made with electrolytic and silicothermic manganese are given in Table 2 and plotted as a function of cold-work in Fig. 1. In comparing these two alloys it should be noted that they differ in annealed or ready-to-finish grain size although both were treated by the same schedules. This difference in grain size can account, in part, for the higher strength and hardness and lower ductility of the silicothermic manganese alloy compared with the electrolytic manganese alloy. It cannot be considered a complete explanation, however, since the restricted grain size doubtless stems from the impurities in the silicothermic manganese and these can have other effects as well.

The silicothermic manganese alloy as annealed for 1 hr. at 1200°F. with an 0.010-mm. grain is about 12,000 lb. per sq. in. higher in tensile strength and 17,000 lb.

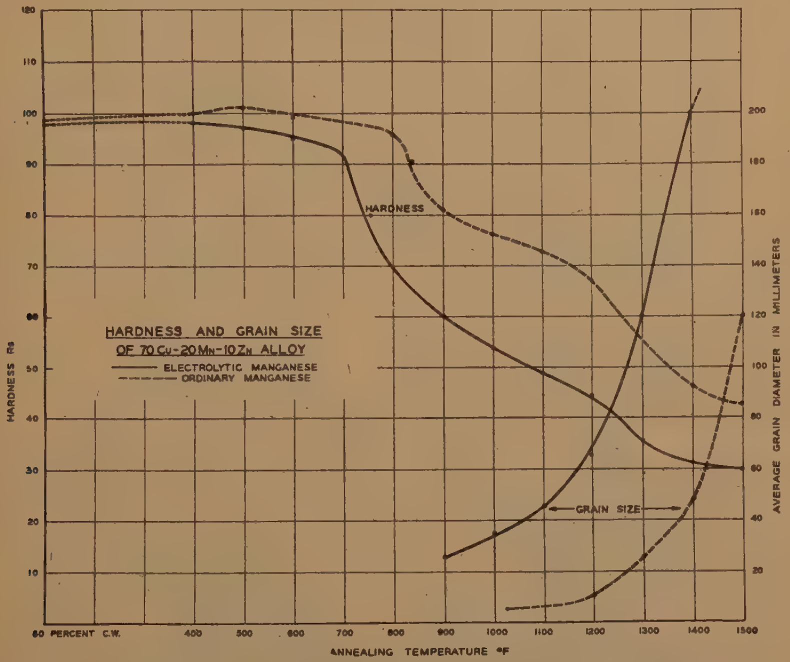


FIG. 3.—VARIATION OF HARDNESS AND GRAIN SIZE WITH ANNEALING TEMPERATURE.

per sq. in. higher in yield strength than the pure manganese alloy and maintains these differentials to somewhere between 40 and 60 per cent reduction upon cold-working. Beyond this point the differentials decrease but are still significant at 80 per cent reduction. The electrolytic manganese alloy has higher elongation and lower hardness as annealed. These differences decrease rapidly on working and are not significant beyond 40 per cent reduction.

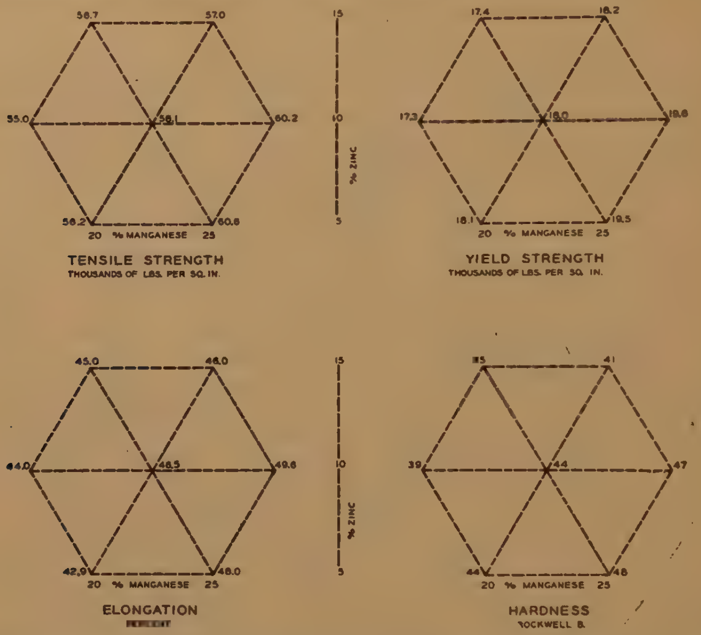
TABLE 2.—*Variation in Physical Properties with Cold-work*

Alloy	Reduced in Thickness by Rolling, Per Cent	Tensile Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In. 0.2 Per Cent Offset	Elongation, Per Cent	Hardness, Rockwell B
Electrolytic manganese, 70 Cu, 20 Mn, 10 Zn.	0	58,100	18,000	46.5	44
	20	72,500	62,000	16.0	84
	40	89,500	86,500	3.9	93
	60	101,500	99,000	2.8	98
	80	108,500	104,500	2.5	101
Ordinary manganese, 70 Cu, 20 Mn, 10 Zn.	0	70,100	35,000	32.5	67
	20	85,000	80,500	10.5	90
	40	99,500	95,500	3.5	96
	60	108,000	103,000	2.5	99
	80	117,000	108,000	2.3	101

The mechanical properties obtained by annealing 60 per cent cold-reduced material for 1 hr. at various temperatures are shown in Table 3 and plotted against temperature in Figs. 2 and 3.

The normal recovery, recrystallization, and grain-growth effects are evident in the tensile strength, yield strength, elongation, hardness, and grain-size curves for the electrolytic manganese alloy. From these curves it is obvious that recrystallization has taken place between 700° and 800°F. This temperature is somewhat higher than for copper-zinc alloys under similar conditions, but this is not unexpected, considering the fact that we are dealing with a ternary alloy. The grain growth does not appear to be inhibited by the presence of manganese but is normal and, as shown in Fig. 3, the grain size increases regularly from 0.010 mm. at 800°F. to 0.200 mm. at 1400°F.

The property differences noted between electrolytic and silicothermic manganese alloys as cold-worked are also reflected in the annealed material. The impure alloy consistently maintains higher strength and hardness over the temperature range examined. The elongation and grain size remain well below those of the electrolytic alloy at each temperature.



TENSILE STRENGTH
THOUSANDS OF LBS. PER SQ. IN.

YIELD STRENGTH
THOUSANDS OF LBS. PER SQ. IN.

ELONGATION

HARDNESS
ROCKWELL B.

FIG. 4.—MECHANICAL PROPERTIES OF ALLOY NO. 1 AND ALLOYS 3 TO 8 INCLUSIVE AFTER ANNEALING ONE HOUR AT 1200°F.
Average values plotted according to nominal composition on ternary coordinates.

In addition to these differences in properties of the two alloys, there are pronounced irregularities in the property curves for the silicothermic manganese alloy. These are reproducible and consistent and are associated with overlapping effects of aging, stress relieving, recrystallization, restricted grain growth, and normal grain growth.

As previously noted, these differences are due partly to grain size and partly to the impurities introduced by the silicothermic manganese. The influences of grain size and impurities cannot be evaluated separately nor can the effects of the individual impurities be stated. However, several effects noted can be attributed to the impurities rather than to grain size. These are the low-temperature aging, the high-recrystallization temperature, the restricted grain growth, and differences in elongation noted at equivalent grain sizes.

The aging effects in the impure alloy annealed for 1 hr. at 400° to 600°F. (Fig. 2) are much more pronounced than in the pure manganese alloy. These increase of 5000 lb. per sq. in. in tensile strength and 6000 lb. per sq. in. in yield strength are due to precipitation of impurities and not to grain size. The finer grain sizes merely aid the precipitation and hence accentuate the effects. The presence of a precipitate is further indicated by the higher recrystallization temperature and restricted grain growth encountered in this alloy. Recrystallization takes place between 800° and 900°F., as indicated by the property curves and confirmed by the microstructures. This is 100°F. above the temperature for the pure alloy instead of being lower, as might be expected. A material with small grain size should recrystallize at a temperature below that of similarly cold-worked metal of large grain size because small-grain metal necessarily requires more energy for deformation, and this stored-up energy is available to assist in reaching the internal-energy requirements of recrystallization. These requirements will thus be met at a lower thermal input; consequently, recrystallization will take place at a lower temperature. It is obvious, therefore, that the higher temperature noted is attributable to some obstruction, such as a precipitation of impurities in grain boundaries and slip planes, which interferes with normal recrystallization. Such obstructions to the diffusion processes necessary for recrystallization will increase the energy requirement for recrystallization and necessitate higher temperatures.

TABLE 3.—*Variation in Physical Properties with Annealing Temperature*

Alloy	Annealing Temperature, Deg. F.	Ultimate Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In. 0.2 Per Cent Offset	Elongation, Per Cent	Hardness, Rockwell B
Electrolytic manganese 70 Cu, 20 Mn, 10 Zn	As rolled	101,500	99,000	2.8	98
	400	103,000	99,500	3.3	98
	500	97,500	92,500	4.5	97
	600	90,000	83,000	8.0	95
	700	85,000	75,500	10.0	93
	800	68,300	36,100	33.5	69
	900	65,300	28,500	39.0	60
	1000	63,400	24,200	40.0	54
	1100	61,200	20,400	43.0	49
	1200	58,100	18,000	46.5	44
	1300	54,500	15,800	48.5	35
	1400	52,400	15,100	49.0	31
	1500	49,000	14,200	46.5	30
Ordinary manganese 70 Cu, 20 Mn, 10 Zn	As rolled	108,000	103,000	2.5	99
	400	109,500	108,000	3.0	100
	500	113,000	109,000	2.6	101
	600	108,500	107,000	3.1	99
	700	101,000	93,500	8.3	98
	800	95,900	87,500	9.1	96
	900	77,000	53,400	25.0	80
	1000	74,000	46,000	28.5	76
	1100	73,000	42,000	30.5	73
	1200	70,100	35,000	32.5	67
	1300	65,000	22,100	35.0	55
	1400	60,500	19,000	34.5	46
	1500	52,600	17,000	40.0	42

Although recrystallization is complete below 900°F., grain growth is not evident in the 900° to 1200°F. temperature range, and the grain size remains below 0.010 mm. This introduces irregularities in the slope of the property curves of Fig. 2 in this temperature range. The grain-size curve does not parallel that of the pure alloy until 1300°F. has been exceeded. It is suggested that this slow rate of growth is due to precipitation of impurities below 900°F. and that they are active barriers to grain growth until redissolved at temperatures exceeding 1300°F. Similar grain-growth characteristics have been noted in other silicothermic manganese alloys made in these laboratories.

If the properties of these two alloys are compared at the same grain size—at 0.045 mm., for example—we find that they have essentially the same tensile strength (61,200 to 60,500 lb. per sq. in.), yield strength (20,400 to 19,000 lb. per sq. in.), and hardness (Rockwell B-46 to B-49), but that they differ in elongation. The electrolytic manganese alloy has an elongation 8.5 per cent greater than that of the silicothermic manganese alloy (43 per cent to 34.5 per cent). This great difference in elongation accompanied by essentially equal strength and hardness at equivalent grain size must be due necessarily to an alloying effect produced by the impurities present in the silicothermic manganese.

The effects of the impurities may be summed up as: (1) restrictions imposed on grain size and, (2) alloying effects. The combination of these two factors produces the higher strength, greater hardness, and lower elongation found in the silicothermic manganese alloy.

EFFECTS OF COMPOSITION

The properties of alloys 3 to 8, inclusive (Table 1), do not vary greatly from those of the central alloy. This relative insensitivity to variations in composition is surprising, considering the relatively large range of composition covered. In general, there are small but definite trends of increasing strength, hardness, and elongation with increasing manganese content. These are illustrated in Fig. 4, in which the data for material annealed 1 hr. at 1200°F. are graphically represented on ternary coordinates according to nominal composition. These trends are consistent, regardless of whether copper or zinc is maintained constant. Variations in copper and zinc with constant manganese do not appear to be significant, except for a somewhat low value for elongation for alloy No. 3. Although this difference is not great, and the data are insufficient to warrant definite conclusions, it should be noted that this particular alloy has the highest residual aluminum content.

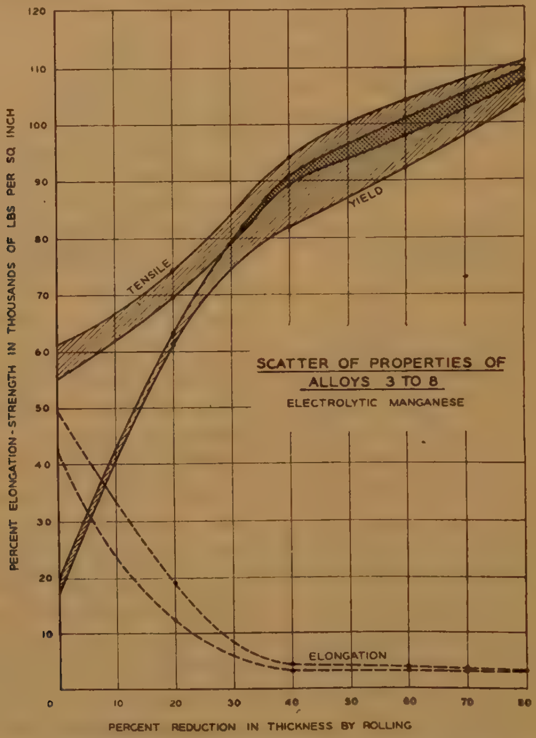


FIG. 5.—SCATTER OF AVERAGE TENSILE STRENGTH, YIELD STRENGTH, AND ELONGATION FOR ALLOYS 3 TO 8 IN THE COLD-WORKED CONDITION.

The maximum and minimum properties for the entire group of alloys for each condition of cold-working are shown in Fig. 5. This method of representation was chosen because the small differences in properties made it impractical to plot the individual characteristics of each alloy. Data obtained on material that had been cold-reduced 60 per cent and then annealed for one hour at various temperatures are plotted in the same manner in Fig. 6. These curves are quite similar to Figs. 1 and 2; they show the magnitude of the variation in properties that may be expected in this range of composition. Upon cold-rolling the tensile strength does not vary more than ±4000 lb. per sq. in. from the average of the group, regardless of the amount of cold-work, while the yield-strength variation increases from ±1000 lb. per sq. in. at 20 per cent cold reduction to ±4000 lb. per sq. in. at 40 per cent and beyond. The elongation varies ±3.5 per cent from the group average at 20 per cent cold work and less than ±1 per cent at 40 per cent and higher. Upon annealing, variations of ±3000 lb. per sq. in. tensile strength, ±5000 lb. per sq. in. in yield strength, and ±4 per cent in elongation were observed.

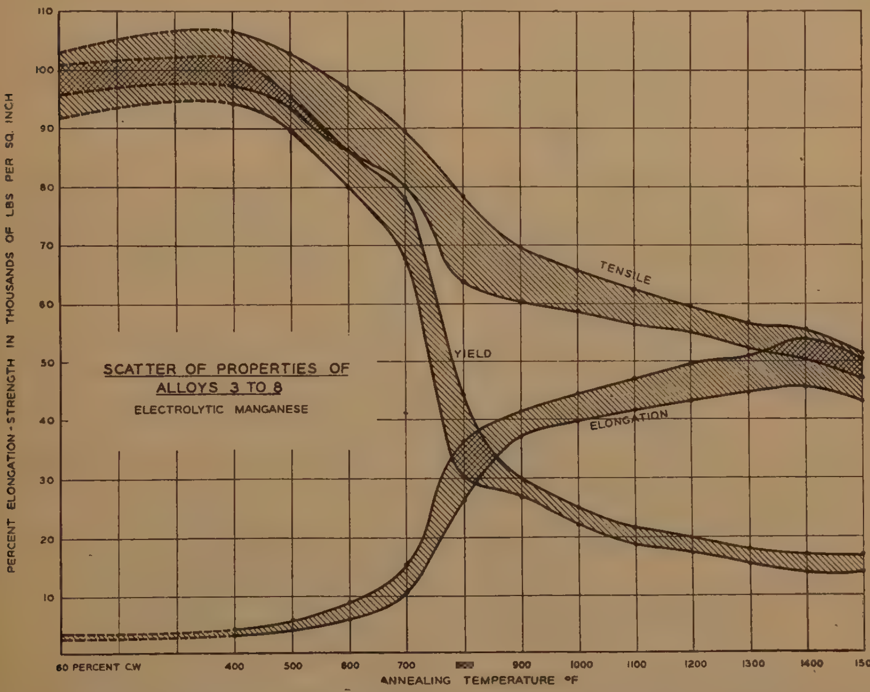


FIG. 6.—EFFECT OF ANNEALING TEMPERATURE ON RANGE OF AVERAGE TENSILE STRENGTH, YIELD STRENGTH, AND ELONGATION OF ALLOYS 3 TO 8 INCLUSIVE.

COMPARISON WITH SEVERAL COMMERCIAL ALLOYS

For the purpose of comparison of the properties with those of this manganese brass, data on four common high-copper alloys are listed in Table 4. These data were obtained from published graphs and represent rounded averages for 0.040-in. sheet with a ready-to-finish grain size of 0.070 mm. From the values given for the electrolytic manganese alloy in Table 2 it is evident that this alloy is considerably harder and stronger than the commercial bronze although it has the same ductility. It is also harder and stronger than he cartridge brass although it does not possess the same elongation. The manganese alloy work-hardens faster than either of the brasses, consequently the differences in strength become even greater upon cold-working without significant losses in ductility.

The properties of the manganese brass approach more closely those of the white alloys given in Table 4. It is slightly harder and stronger than the cupronickel and has greater elongation, particularly in the annealed and mildly cold-worked condition. It is also slightly stronger than the nickel silver and has approximately the same hardness and elongation, while its work-hardening rate is essentially the same.

TABLE 4 —*Physical Properties of Commercial Bronze, Cartridge Brass, Cupronickel and Deep Drawing Nickel-silver**

Alloy	Reduction in Thickness by Rolling, Per Cent	Tensile Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In. 0.2 Per Cent Offset	Elongation, Per Cent	Hardness, Rockwell B
Commercial bronze (90 Cu, 10 Zn).	0	35,000	8,000	47	
	20	48,000	43,000	11	50
	40	58,000	57,000	5	68
	60	68,000	64,000	3.5	76
Cartridge brass (70 Cu, 30 Zn).	0	48,000	15,000	65	10
	20	74,000	55,000	22	73
	40	90,000	71,000	8	84
	60	101,000	82,000	4	90
Cupronickel (70 Cu, 30 Ni).	0	52,000	15,000	38	30
	20	68,000	67,000	8	76
	40	78,000	76,000	3	83
	60	85,000	82,000	3	86
Nickel silver (66 Cu, 18 Ni, bal. Zn).	0	52,000	18,000	40	36
	20	63,000	51,000	12	70
	40	76,000	75,000	3	85
	60	91,000	90,000	3	90

* Average values taken from curves presented in Copper and Copper Base Alloys, by Wilkins and Bunn.

SUMMARY

1. The mechanical properties of a white, high-strength, single-phase alloy of 70 per cent copper, 20 per cent manganese, 10 per cent zinc, as affected by cold-rolling and annealing, have been determined.

2. When made with electrolytic manganese, the alloy in the annealed condition (0.065-mm. grain size), has a tensile strength of 58,100 lb. per sq. in., a yield strength of 18,000 lb. per sq. in. with an elongation of 46.5 per cent and a hardness of Rockwell B-44.

3. After 80 per cent reduction in thickness, the tensile strength increases to 108,000 lb. per sq. in., the yield strength to 104,000 lb. per sq. in., with an elongation of 2.5 per cent and a hardness of Rockwell B-101.

4. If the alloy is made with silicothermic manganese, it is stronger, harder, and less ductile than when made with electrolytic manganese.

5. The normally associated impurities in silicothermic manganese produce an aging effect in the 400° to 600°F. range, raise the recrystallization temperature, and restrict the normal grain growth in the 1000° to 1200°F. temperature range.

6. The properties of adjacent compositions indicate the alloy to be insensitive to relatively large variations in composition.

7. The alloy is slightly stronger and harder than straight alpha brasses and compares favorably in mechanical properties with nickel silver and other common high-copper alloys.

Oxidation Inhibitors in Core-sand Mixtures for Magnesium Castings

By O. Jay Myers,* Member A.I.M.E.

(Cleveland Meeting, October 1944)

The war effort has furnished the necessary impetus for better magnesium foundry practice. Four or five years ago, there were but a few formulas in general use for core-sand mixtures for magnesium castings. Certain sands, binders, and inhibitors were specified and the proportions of these materials in each mixture were maintained between very narrow limits. As more and more war industries entered the field, much research was carried out and methods and practices were improved.

Magnesium founding is still in a state of flux; therefore it is not uncommon to find one foundry spraying inhibitors on its cores, and another foundry using sand mixtures with incorporated protective agents.

The basic core or dry-sand mold mixture for magnesium in use today is compounded with sand, core oil or resin binder, cereal, and moisture. Core oil or resin binder are added for baked strength while the cereal binder and moisture are for green strength. The normal mixtures (based on the weight of the sand) contain from 0.5 to 1.5 per cent of both cereal binder and core oil, and the moisture content varies between 1.5 and 5 per cent. The ratio of core oil to cereal binder varies from 60:40 to 40:60, while the correct amount of moisture depends upon the method of coremaking.

PROTECTIVE AGENTS

In all magnesium practice, protective agents are used in conjunction with the core and molding sands to prevent oxidation of the metal. The use of these inhibitors is not novel, but publications covering this field are not entirely adequate. Beck[1] says:

> Magnesium alloys decompose water to form magnesium oxide, hydrogen being liberated in the process ($Mg + H_2O \rightarrow H_2\uparrow + MgO$). This reaction results in the blackening of the skin and the ppearance of areas of porosity on the casting surface. the cavities of which are filled with a grey oxide powder (these are termed 'burns').

Although sand cores for magnesium castings are thoroughly dried during the baking cycle, burning will take place on the castings unless the metal is protected properly. This type of burning is more difficult to define than the "water-magnesium" reaction cited by Beck. A possible explanation may lie in the following equation:

$$2Mg + O_2 \rightarrow 2MgO$$

Here, the source of the oxygen is not water, but the air in the mold cavity, together with the chemically combined oxygen in the core-binding media.

Generally, two methods are used to prevent this reaction from taking place.

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* Metallurgist, Wright Aeronautical Corporation, Lockland, Ohio.

[1] A. Beck: The Technology of Magnesium and its Alloys, 324. F. A. Hughes and Co.

One practice is to spray the surfaces of the baked core and the dry sand mold with a solution of inhibitors; another is to incorporate protective chemicals in the sand mixtures before baking. In either case the air in the mold cavity may be flushed out with sulphur dioxide, to minimize burning.

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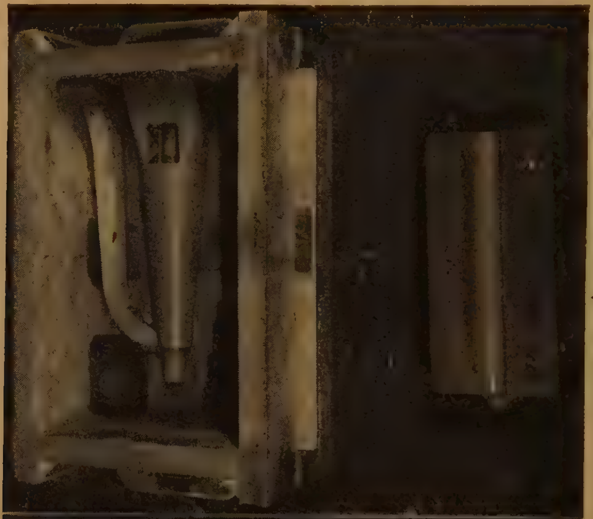

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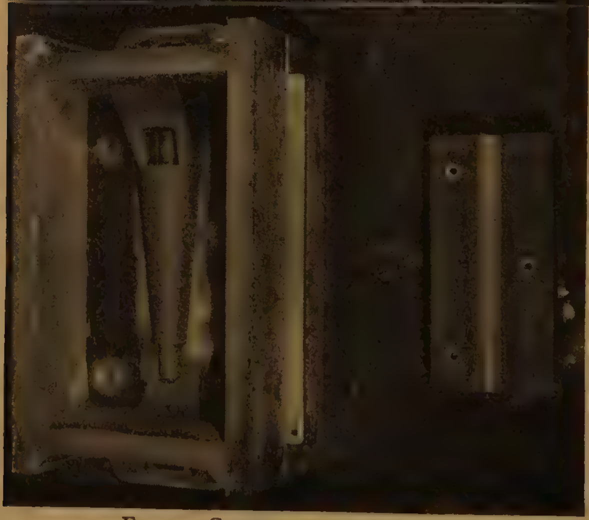

Fig. 1.—Core pattern equipment.
Fig. 2.—Drag pattern equipment.

Sulphur, boric acid, and fluoride salts are the most commonly used inhibitors. When baked cores and molds are sprayed, fluorides are used, since these salts are water-soluble. Generally, combinations of ammonium acid fluoride, ammonium borofluoride, and ammonium silicofluoride are made for this purpose. They are not usually mixed in the core sand, for the following reasons:

1. The green strength of the mixture is lowered, causing an increase in "stickiness."

2. Metal pattern equipment is easily corroded by the ionized salts.
3. Coremakers may contract dermatitis.
4. Most fluorides are easily sublimed during core baking.
5. The baked strength of the mixture is depressed considerably.

Instead of combining the fluorides in the original sand mixture, the baked cores and molds are sprayed with a 10 to 20 per cent solution of fluorides in water, after which they are dried in a "spray dry oven" and stored in a constant-humidity room until used.

The disadvantages of this practice are many:

1. The fluoride spray is a health hazard.
2. Casting protection is not uniform.
3. The spray must be oven-dried on the cores.
4. Moisture absorption from the atmosphere makes it necessary to store the cores in a constant-humidity room.
5. The fluoride spray corrodes the surface of the baked core and destroys the smooth rammed skin unless the original core is extremely hard and strong.
6. Spraying is an added operation.

An intimate blend of sulphur and boric acid may be advantageously incorporated in core-sand mixtures in moderate quantities if the cores are baked at temperatures not in excess of 400°F. If used in this manner, they possess the following advantages:

1. The green compressive strength of the core-sand mixtures is increased.
2. The baked tensile strength of the sand mixture is not decreased appreciably.
3. They are inexpensive and readily available.

All inhibitors possess one disadvantage; namely, their relative ease of sublimation. The most economical method of using sulphur and boric acid in a core sand is to incorporate them during mixing and then bake them at low temperatures for a relatively short length of time.

Physical Properties of Core-sand Mixtures

The physical properties of such core-sand mixtures may vary between very wide limits, depending upon the sizes and shapes of the castings founded. For practical uses, the minimum and maximum values are as follows:

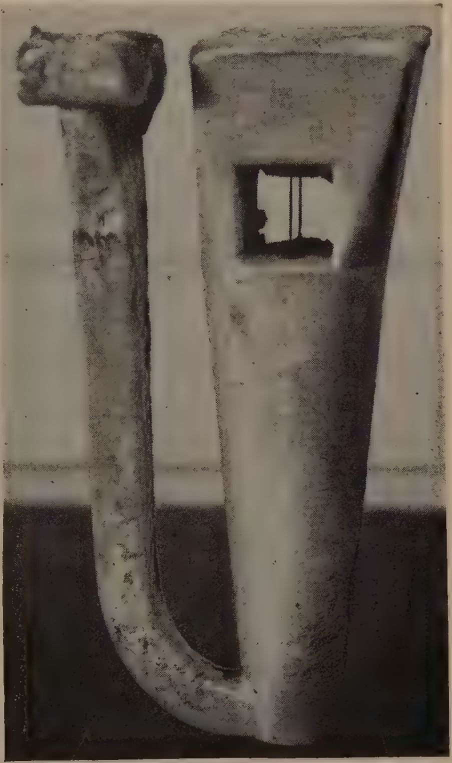

FIG. 3.—TYPICAL CASTING AFTER KNOCKOUT.

	Min.	Max.
Moisture, per cent	1.5	5.0
Green compression, lb. per sq. in.	0.5	1.25
Baked tensile, lb. per sq. in.	100	200

Low moisture contents are usually employed when the cores are made on a core-blow machine; higher moisture contents are used for hand-ramming cores. Green compression values in excess of 1.0 lb. per sq. in. are necessary only for the more intricate shapes of cores, especially where there is much sand "overhang."

Tensile strengths of less than 100 lb. per sq. in. can produce high baked-core scrap unless the cores are carefully handled. Cracked castings may be caused by cores that are too strong.

The basic blow-machine sand contained the following ingredients:

1000 lb. round-grained Ottawa-type silica sand (G.F.N. 62–65),
12 lb. cereal binder,
12 pt. low-baking-temperature core oil,
1.5 per cent moisture.

All of the facing sand in the mold was mixed in 25-lb. batches in the laboratory muller. The mixing time was 2 min. dry, 3 min. with water, and 3 min. with oil. The cores were hand-rammed and baked in a laboratory gas-fired oven for 3 hr. at 350°F. Tensile briquettes accompanied each mold in the oven (Fig. 4).

A standard method was developed for pouring the castings from production superheating pots. The temperature of the metal varied between 1350° and 1375°F. when poured.

The cooled castings were knocked out of their molds and sandblasted. The sprues and risers were cut off by band-

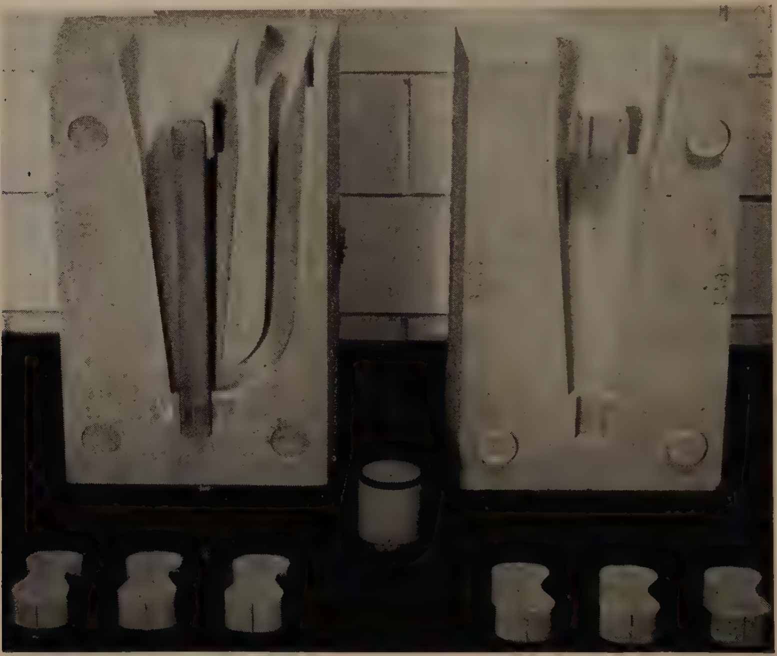

FIG. 4.—BAKED CORE AND DRY SAND MOLDS AND TEST SPECIMENS.

EXPERIMENTS WITH MIXTURES

The basic sand mixture chosen for this project was a typical heavily bonded blow-machine core-sand mixture. A small mold pattern was constructed to provide the necessary cores for a hollow, truncated conical casting (Figs. 1 and 2). The altitude of the casting is 8 in., the base is 3 in. in diameter and the top 1½ in. This cone envelopes a pencil core of 1-in. diameter. The volume of the casting is approximately 27 cu. inches.

Preliminary gating and risering experiments demonstrated that the best method to found the casting was to pour it vertically. The gate entered the small (½-in.) section of the mold and risers were taken off the large (1-in.) section (Fig. 3).

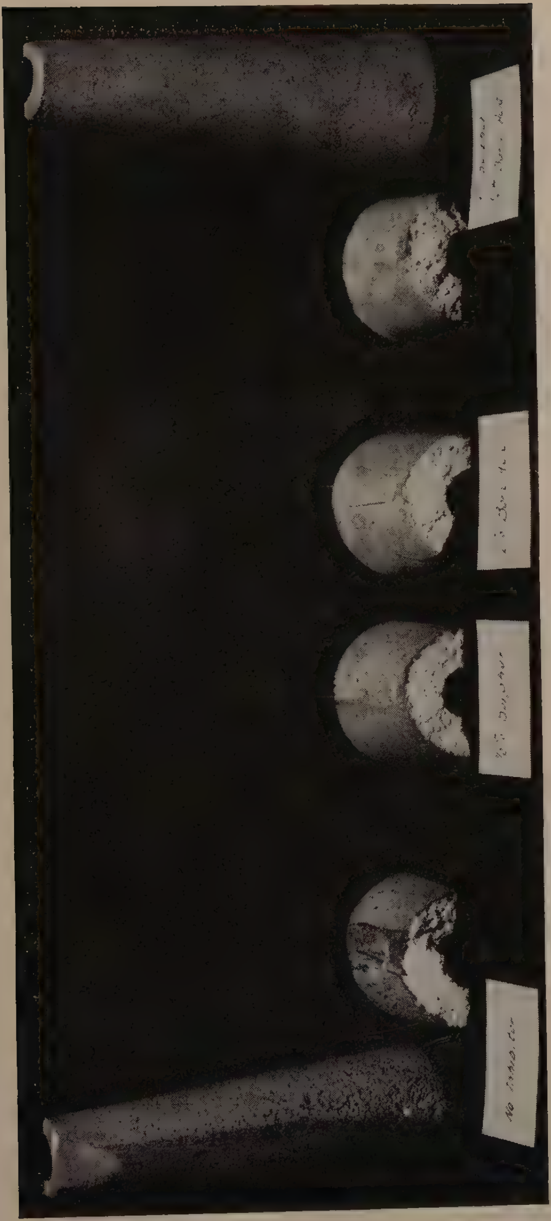

FIG. 5.—TYPICAL SURFACE AND FRACTURE CONDITIONS.

saws, after which the castings were sawed lengthwise. One half of each casting was cleaned on an abrasive wheel and then X-rayed; the other half was fractured. Metallographic specimens of a few castings were prepared and examined microscopically.

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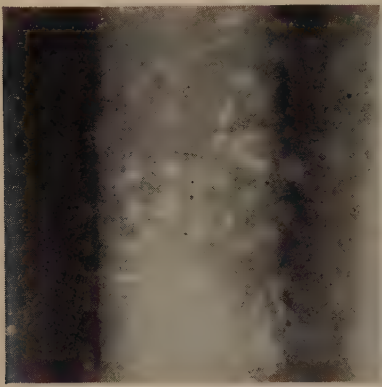

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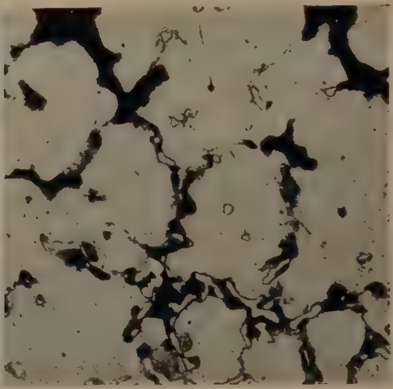


Fig. 6.—Radiographic print of severe internal burning.

Fig. 7.—Burning caused by insufficient protection of metal. As cast. × 100. Nital etch.

Twenty sand mixtures were made, each one of which contained a different percentage of inhibitor added to the basic formula.

The first casting was founded in the basic mixture without inhibitor addition. It exhibited heavy skin burning and at knockout burned sand was observed clinging to the casting. Sandblasting revealed numerous pits on the casting surface (Fig. 5). Radiographs showed internal burning (Fig. 6) and the fractured surface was filled with vesicles. Heavy interstitial burning was evident from metallographic examination, as shown in Fig. 7.

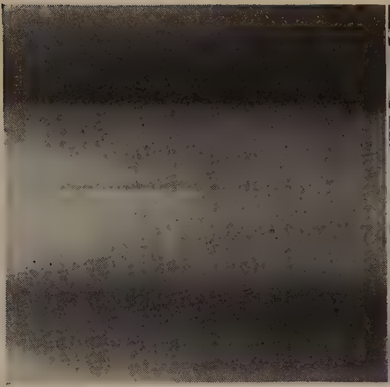
In the next test, 0.5 per cent sulphur (by weight of the sand) was added to the basic mixture. The knockout qualities of this casting were similar to those of the first one, but sandblasting and further investigation revealed a definite reduction in the amount of burning (Fig. 5). The protection was still inadequate.

Sulphur was added to subsequent basic sand mixtures in amounts of 1 per cent and 1.5 per cent, with no noticeable improvement in casting. The addition of this quantity of agent reduced both the baked tensile and the green compressive strength of the sand mixture.

When a 2.5 per cent addition of sulphur was used, the casting showed a definite improvement over any of those previously founded. Severe burning was reduced to a minimum, but the surface of the metal was still covered with charred sand and binder when knockout results were examined.

Both the tensile strength and the green compression of the sand mixture were reduced by 5 per cent sulphur but the casting was not improved.

The first series of mixtures made to determine the effect of boric acid contained 0.5 per cent of this chemical. The casting was as satisfactory as any of those previously made. It broke completely free from the mold at knockout and showed only a slight skin discoloration and no pits on the surface (Fig. 5). Radiographs revealed no serious internal burning (Fig. 8) and microscopic examination showed a definite reduction of porosity (Fig. 9).

8 

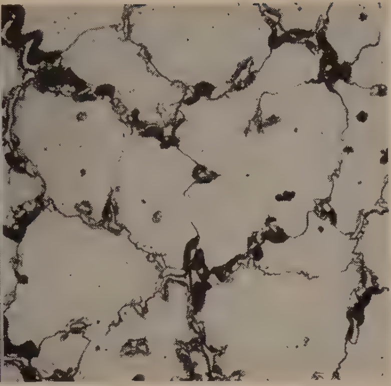
 9

FIG. 8.—RADIOGRAPHIC PRINT OF CLEAN CASTING.

FIG. 9.—MICROSTRUCTURE OF CASTING FOUNDED IN SAND CONTAINING 0.5 PER CENT BORIC ACID. AS CAST. × 100. NITAL ETCH.

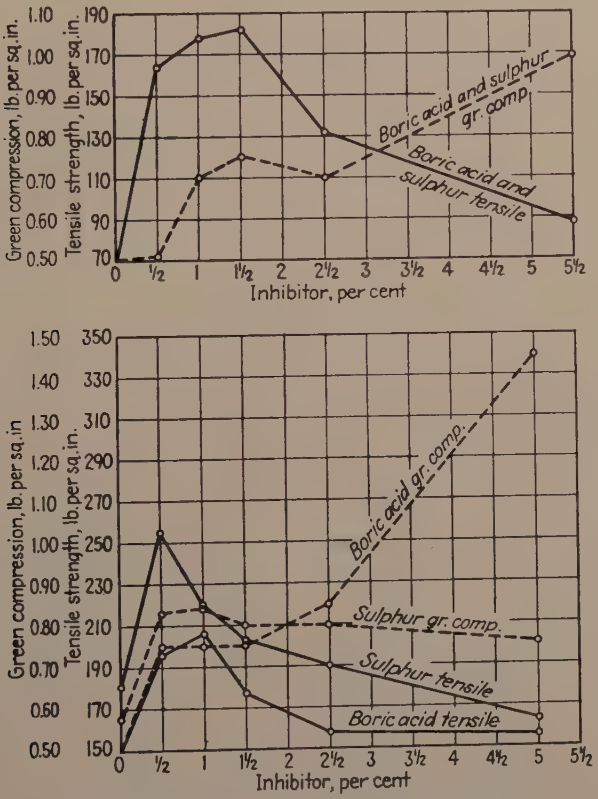


FIG. 10.—PHYSICAL PROPERTIES OF SAND MIXTURES.

When increasing amounts of boric acid were used (1 and 1.5 per cent), the tensile strength of the baked sand mixture dropped while the green compression became slightly greater. No casting improvement was noted.

A satisfactory casting was produced when 2.5 per cent boric acid was added to the basic sand mixture, but gas was observed emanating from the risers when the metal was poured.

The core hardness and baked tensile strength of the sand mixture were reduced by 5 per cent boric acid but its green compression was increased greatly. The casting was unsatisfactory. It was exceedingly difficult to separate the mold from the casting at knockout. This may be attributed to the violent gas evolution from the risers during the pouring of the metal. The pressures set up in the risers during the foaming and frothing of the metal may have caused the metal to penetrate the soft surface of the core. A possible explanation for the gas evolution may be based on the following equations:

$$2H_3BO_3 \rightarrow 3H_2O + B_2O_3 \qquad [1]$$

$$H_2O + Mg \rightarrow H_2 + MgO \qquad [2]$$

The first reaction results from the breakdown of the boric acid in the mold at pouring temperatures. The second reaction is the same as that mentioned by Beck,[1] the source of the water being boric acid decomposition, not the moisture in the mold. The casting fracture was drossy and full of skin inclusions.

Magnesium foundry practice generally admits that both sulphur and boric acid should be used in core-sand mixtures. For this reason, several castings were poured in molds containing an equally divided combination of these chemicals.

A casting was poured in a mold containing 0.25 per cent of boric acid and 0.25 per cent sulphur by weight of the sand. The casting broke free from the mold (Fig. 5) but X-ray examination showed excessive dross trapped in the metal, confirmed in fracture. The pencil core left a spotty, bluish skin on the internal surface of the casting. When 0.5 per cent of each ingredient was used in the sand mixture, the casting was satisfactory.

All subsequent additions of sulphur and boric acid were made simulating the total amount of inhibitors present in the sulphur and boric acid tests. All castings were acceptable except the one for which 2.5 per cent of each agent was used. As the percentages of inhibitors were increased, the physical properties of the sand dropped far below optimum workability.

TABLE 1.—*Effects of Inhibitor Additions*

Type of Inhibitor	Percentage of Inhibitor Used by Weight of Sand	Tensile Strength, Lb. per Sq. In.	Green Compression, Lb. per Sq. In.	Casting Results
None	None	182	0.58	Very poor
Sulphur.....	0.5	255	0.83	Poor
Sulphur.....	1	220	0.84	Poor
Sulphur.....	1.5	203	0.80	Poor
Sulphur.....	2.5	190	0.80	Fair
Sulphur.....	5	163	0.75	Fair
Boric acid...	0.5	197	0.75	Good
Boric acid...	1	206	0.75	Good
Boric acid...	1.5	177	0.75	Good
Boric acid...	2.5	158	0.85	Fair
Boric acid...	5	156	1.45	Poor
Sulphur.....	0.25	164	0.52	Fair
Boric acid...	0.25			
Sulphur.....	0.5	178	0.70	Good
Boric acid...	0.5			
Sulphur.....	0.75	182	0.75	Fair
Boric acid...	0.75			
Sulphur.....	1.25	132	0.70	Fair
Boric acid...	1.25			
Sulphur.....	2.5	88	1.00	Poor
Boric acid...	2.5			
NH_4SiF_6.....	0.5	148	0.48	Good
NH_4SiF_6.....	1	119	0.30	Good
Diethylene glycol.....	0.5	190	0.35	Fair
Boric acid...	0.5	135	0.45	Fair
NH_4SiF_6.....	0.5			

When 0.5 per cent of ammonium silicofluoride was incorporated in the sand mixture, the casting was as well protected as any of those previously made. The surface was clean and the fracture was bright. The addition of this salt, however,

considerably lowered the green compression and tensile strength of the sand mixture. When one per cent of ammonium silicofluoride was used, no great difference in protection could be noted.

Diethylene glycol (0.5 per cent by weight of the sand) gave some protection to the casting. An attempt to combine this material with a low-baking-temperature core oil for magnesium foundry practice might prove profitable.

When 0.25 per cent boric acid and 0.25 per cent ammonium silicofluoride were both added to the basic sand formula, the casting showed no better qualities than if each one were used alone.

Table 1 and Fig. 10 sum up the effects of inhibitor additions on the physical properties of core-sand mixtures for magnesium castings.

Although these tests were made on only one type of casting, production results with castings varying from 5 to more than 50 lb. have been gratifying. The foundry core-sand mixture normally contains one per cent of sulphur and one per cent of boric acid. Experimental production tests were made, lowering the total percentage of inhibitor to one per cent, with excellent results. It has been shown that excessive amounts of inhibitors cause gassing and are detrimental. Boric acid is a much stronger inhibitor than sulphur, but when used alone it destroys the desired knockout properties. If sulphur is used as the only agent, surface properties of the subsequent casting are inferior; for this reason, a combination of the two is best.

ACKNOWLEDGMENT

The writer wishes to acknowledge the assistance of the Foundry Materials Laboratory personnel of the Wright Aeronautical Corporation. Special thanks are due to Mr. S. Beliaeff and to Ensign George Hopping, U.S.N.R., for their aid in the compilation of this paper.

DISCUSSION

(*J. D. Hanawalt presiding*)

R. E. WICK.*—This paper is a fine contribution to the science of casting. The results are of special interest since they deal with the all important effect of variations in inhibitor composition.

Was the sand used in these experiments new sand, reclaimed sand, or a mixture? We have made some cores of reclaimed sand using boric acid and sulphur, which yield the desired results.

O. J. MYERS.—The sand used in these experiments was new sand.

MEMBER.—Were the castings as cast or after heat-treatment?

O. J. MYERS.—The castings were not heat-treated.

MEMBER.—Did you make any tests on the retained strength with boric acid only in cores?

O. J. MYERS.—Many tests performed in the laboratory have shown that boric acid increases the retained strength of a magnesium core-sand mixture. Laboratory results have been confirmed in "knocking out" production castings.

A. T. PETERS.†—I would like to ask Mr. Myers a question pertaining to the actual composition of the baked cores used in his tests. We have found that the composition of the inhibitors may change to a marked extent during baking. Almost all of the sulphur may be lost from cores baked at 400°F., and the retained sulphur appears to be a critical function of the baking temperature in the range between 300° and 400°F. Our tests also indicate that boric acid is also lost to some extent during baking and that which remains is apparently converted to boric anhydride. Our analyses indicate that essentially no boric acid remains as such in the baked cores. Can you give us any information on the amount and condition of the inhibitors retained in the cores?

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* Dow Chemical Co., Midland, Michigan.

† Laboratory Technician, The Hydro-Blast Corporation, Chicago, Illinois.

O. J. Myers.—It is a proved fact that at least 50 per cent of the sulphur is lost from the exposed core surfaces during core baking at 375° to 400°F. In all probability, boric acid undergoes a chemical change during the core-baking process. The portion of the boric acid in the sand mixture that is subjected to the direct heat of the baking ovens loses at least one molecule of water.

A. T. Peters.—That is right. We have found that out. Thank you very much.

O. J. Myers.—We have found that resin binders give some protection and not as much inhibitor is needed as with oil binders.

F. N. Rhines.*—Is there evidence that boron is absorbed by the metal itself?

O. J. Myers.—None that I know of.

F. N. Rhines.—It was just an idea of the moment. It might be possible to devise an explanation of the effect of boron if it were to behave as an alloying element that oxidizes preferentially at the surface to form some kind of protective coating.

J. D. Hanawalt.†—Mr. Myers has made some remarks about how boric acid might work. I cannot help but wonder about that a little since boric acid is effective as a protective agent. He indicates that boric acid forms some water, which in turn reacts with Mg to make MgO and H_2. If it did that to a very limited extent, that might be the way boric acid works as an inhibitor, but he used that equation and that idea to explain the foaming and frothing at the sprue. I should not think that boric acid could be responsible for that frothing.

O. J. Myers.—The question concerned the evolution of gases by the breaking down of the boric acid and water. Boric acid breaks down to form boric anhydride and water. In turn the water reacts with magnesium, forming hydrogen, which evolves as a gas.

Member.—I would like to ask Mr. Myers if he has noticed any difference in the amount of porosity at the bottom of the casting as compared with the amount of porosity at the top, because more metal going through the sprue would heat the bottom part of the casting more.

O. J. Myers.—No, I have not noticed any difference in porosity in the two sections of the castings. They were fractured lengthwise. The risers were large enough to obviate shrinkage.

Member.—I meant the amount of burning.

O. J. Myers.—No, I have not found any difference in the amount of burning at the bottom and the top of the casting. In spite of the fact that there is a greater opportunity for "burning" at the gate than at the riser, the presence of an adequate amount of inhibitor prevents this phenomenon from occurring. As the sand heats up at the gate (from metal flow) more inhibiting gases are evolved and more protection is afforded the molten magnesium.

Member.—Instead of using boric acid and sulphur, was any mixture made with borax, sulphuric acid and sulphur, which in some foundries is used for sand protection? If any such mixtures were used in the cores, what effect, if any, was there with the boric acid made in this way compared with using boric acid as a natural product?

O. J. Myers.—No mixtures were made with the two inhibitors mentioned. I know a mixture is being used, but I believe only in molding sand. If you introduce sulphuric acid and borax in a core-sand mixture, the sulphuric acid would immediately attack the cereal binder and depress the green strength, and for core-sand workability green strength is necessary.

Member.—Would you prefer to use a mixture of borax and sulphuric acid instead of boric acid, or vice versa, in order to get the best results? What I am trying to find out is, how you regard the formation of sulphates in the resulting changed physical properties of the sand.

O. J. Myers.—We have tried magnesium sulphate as an inhibitor in core sand. The green strength of the sand mixture was lowered. I do not believe that adequate protection can be afforded by just 0.5 per cent of sulphur and boric acid, since moisture is present in the molding sand. In order to inhibit the action of the magnesium with the water in the molding sand a strong inhibitor is needed.

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* Assistant Professor of Metallurgy, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

† Director of Metallurgical Dept., The Dow Chemical Co., Midland, Michigan.

Member.—We realize that as permeability increases, and provided the physical properties of the core remain the same, there is an improvement in shakeout qualities due to the better heat transfer. I wonder if any work was done on the effect of permeability in relation to the inhibitors.

O. J. Myers.—No, we attempted to maintain all variables except the inhibitors constant for this test. We tried to leave it as much constant as possible, so we would be able to know what the inhibitor did. We know from dilatometer tests, however, that your statement is perfectly true. A sand mixture will collapse much more readily when a coarse base sand is used than when a fine base sand is employed, providing the tensile strength and other physical properties are the same.

Member.—What is your opinion of the effect of permeability in relation to the inhibitors?

O. J. Myers.—I believe that the lower the permeability of the sand, the more inhibitor is necessary.

J. C. DeHaven.*—We have not done much with core binders in this work. We have come across a few things. One is the effect of the shape of the sand grain on the tensile strength of the core. I would like to ask Mr. Myers if he noticed that he gets lower baked tensile strength with a subangular or angular grain than with a round grain?

O. J. Myers.—In core sand, yes. The core strength varies almost directly with the angularity of the grain. The round grains have less surface area, therefore, for a certain unit of core oil or other binder, you can cover a round grain more completely than an angular grain.

J. D. Hanawalt.—This matter of the inhibiting agents used in casting magnesium is a fundamental problem and one of practical importance in the magnesium industry. I think of the A.I.M.E. as an organization where our people are trying to get at the fundamentals in metallurgical problems and I believe one of the values of this paper would be to call the attention of the A.I.M.E. organization to this problem.

I believe that less than 20 years ago it was not possible to cast magnesium in green sand. The action and the effects of sulphur, boric acid and fluorides have all been discovered within that period, but there is still plenty of room for improvement, and perhaps if we knew more exactly how these agents worked more advancement could be made.

It is one of the things in the magnesium foundry that requires a little added expense and a little extra care and attention. Something that worked better with less attention would be worth while.

H. L. Grange.*—Mr. Myers, I would like to ask you, and the audience as well, if you have worked with sodium fluoborate and potassium fluoborate. I understand that these compounds, unlike the ammonium fluoborate, do not decompose appreciably at core-baking temperatures. Has anyone had experience with them?

O. J. Myers.—I have not, but I am always glad to hear of new inhibitors being tried.

Member.—In that you might find some better clue as to your reduction of burning. There is a possibility that it may be in there.

O. J. Myers.—Burning can be reduced by the use of magnesium chloride.

Member.—Would Mr. Myers care to comment on his opinion as to whether the pitting could be caused from oxygen taken away from the silica?

The fluxing of a pot where sulphur and boric acid mixed half and half are used, before the cap is put on for superheating, gives a relatively tough film of, I presume, oxide. Could the inhibiting obtained from sulphur and boric acid be the formation of a tough film at the pattern surface, so that the magnesium cannot react with the silica of the sand?

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* Battelle Memorial Institute, Columbus, Ohio.

* Research Metallurgist, Research Laboratories Division, General Motors Corporation, Detroit, Michigan.

O. J. Myers.—Undoubtedly there is some sort of a film formed on the core surface when the casting is properly protected. As shown in the paper, with sulphur that film never is formed. With boric acid, it always is, at least as low as 0.5 per cent boric acid. Fluxing of boric acid and sand is comparatively easily accomplished. Whether the magnesium itself reacts with the sand, I do not know. I know there is no silica pickup in magnesium, but there is some sort of a skin formed between the casting surface and the sand itself.

H. L. Grange.—I agree that a protective skin forms on the casting in the mold. This fact suggests the formation of protective compounds at the surfaces of the metal. The problem of preventing "burning" might be approached from the effect of alloying elements. A. Beck* states that beryllium reduces the tendency of magnesium to oxidize. The effectiveness of an extremely small amount of this element indicates a surface phenomenon. A study of the various elements in the formation of protective skins would contribute greatly to our understanding of the "burning" of magnesium.

I should like to know if anyone is working on the fundamentals of magnesium combustibility. I have attempted to determine the ignition temperature and increased rate of temperature rise of various magnesium alloys by placing them beneath a thermocouple in a combustion tube in which various atmospheres were maintained. These attempts were relatively unsuccessful because the ignition temperature apparently was a matter of chance and could not be reliably reproduced. In regard to the burning of magnesium in sand, one of these tests was made on a sand-covered specimen in an atmosphere of helium. A suppressed type of burning did occur, which would indicate a definite reaction with the silica. I think you will find the tendency of magnesium alloys to burn depends on the alloying elements as well as the mold materials and atmospheres generated by inhibitors.

O. J. Myers.—That is a very interesting point to bring out.

Member.—Silica fluoride breaks down into sodium fluoride and BF_3. There is a gas, and the sodium fluoride is there as a powder. It is quite a complex chemical reaction. I wonder if we couldn't break it down and know that series of inhibitors? If it is not the fluoride, what is it? It is stated in "Beck," which seems to be our authority on many of these problems, that a small amount of a fluoride will inhibit oxidation. With a combination there, maybe that is it. That is why I am thinking in terms of other fluoroborides other than ammonia, because they stand the core-baking process and will be there at the pouring temperature.

Member.—I have found some castings where the core was burnt more on one side than on the other, and on that particular side there was some evidence of gas holes in castings.

From the discussion so far, we could conclude that if the core was burnt there was no inhibitor left in it, and, consequently, no protection for the metal at that particular place; therefore gas formation, with the possibility that gas could not escape and was trapped in the metal, causing gas holes in the finished casting. However, if the core was burnt and no inhibitor left, there was no moisture left either, unless some moisture was picked up by the core before the core was actually placed in the mold.

I wonder what Mr. Myers has to say regarding that.

O. J. Myers.—Was there any burning beside the gas holes?

Member.—No. If there had been burning I would conclude that moisture was present.

O. J. Myers.—The formation of gas holes is another subject completely. We are all troubled with this type of defect constantly and through corrective foundry practice and different experiments with gating and risering of casting. In most cases we are able to eliminate it. The permeability of the sand and of gas-evolving materials in the sand must be controlled.

What was your core-sand mixture? Did you have cereal?

Member.—Yes, an amount of cereal.

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* A. Beck: Technology of Magnesium and Its Alloys, 289. London. F. A. Hughes and Co. Ltd.

O. J. Myers.—We know that gas is given off from cereal, even in the core appearing burned there is likely to be quite a bit of cereal present. By burned core, do you mean completely collapsed?

Member.—Just brown.

O. J. Myers.—There is probably quite a bit of gas-forming material still remaining in the core.

Member.—Without the protection of the inhibitor.

A. T. Peters.—The presence of large amounts of sulphur will contribute toward making a very dark color on a made core, and there may be a relationship between the amount of sulphur and the color of the core, which may be as important as the amount of baking the core has received.

Grain Size and Properties of Sand-cast Magnesium Alloys

By R. S. Busk* and C. W. Phillips*

(Cleveland Meeting, October 1944)

With most cast metals the grain size may vary within wide limits, depending upon the conditions at the moment of freezing. These conditions are subject to control in magnesium-base alloys, by proper melting and superheating techniques, enabling production of quite uniform and fine-grained castings, almost independent of section thickness. However, such variations of grain size as do exist, in common with all metals, are reflected in corresponding changes in mechanical properties. It is the intent of this paper to present data giving the relationship between grain size and mechanical properties. Data are also included on the combined effects of grain size and microporosity. In addition, a short discussion of factors influencing the grain size of sand castings is included.

MEASUREMENT OF GRAIN SIZE

By grain size is meant the statistical distribution of volumes occupied by the individual crystallites in a metal section. Since this is almost always impossible of direct measurement, several methods of estimating and expressing the size have been evolved. Most exact methods make use of the microscope. This involves study of a single plane cut at random through the metal. What is seen in the microscope are polygons, each the cross section of a grain. The diameters or areas of these polygons are then measured and the grain size is expressed as an average diameter, number of grains per unit area, average area per grain, or, rarely, average volume per grain. Rutherford, Aborn, and Bain[3] have discussed extensively the errors involved when using a plane section to estimate volume. They clearly point out that the tendency is to underestimate the true grain size because of the nature of the measurement.

The A.S.T.M. recommends that measurement be made by comparison with a standard chart, by means of Jeffries' planimetric method[4] or Heyn's intercept method. The Society recommends that the notation be in terms of the number of grains per unit area (as is the grain-size number used for steel) or as an average diameter, expressed in inches or millimeters (as for copper and brass).

The method of measurement used for this study was comparison with a standard chart, which has been described by P. F. George.[5] The chart was constructed by photographing at 100 diameters a uniform specimen with an average grain diameter of 0.003 in. The average diameter of this specimen was determined by numerous measurements, using both the Jeffries and Heyn methods. The other grain sizes were then obtained by appropriate enlargement of the master sample.

Careful comparison of the chart method with other methods on identical samples indicates that though the differences be-

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* The Dow Chemical Co., Midland, Michigan.

[3] References are at the end of the paper.

tween methods are small, the chart method tends to indicate slightly larger grain size. Since this is in the direction to more closely approach the true grain size (according to Rutherford), this method is probably to be preferred.

The method of notation used is expression of the average diameter in inches. This follows general nonferrous practice, is direct, and is easily interpreted. For convenience, the numbers used are in thousandths of an inch; thus, a grain diameter of 0.004 in. is given a grain-size number of 4.[5]

EFFECT OF GRAIN SIZE ON PROPERTIES

Preparation of Material

The work reported in this paper is limited to the common sand-casting alloys. Table 1 lists the nominal compositions, together with the typical properties of these alloys. Test bars were obtained by pouring from a crucible containing from 20 to 100 lb. of metal into a green-sand mold. The mold pattern is of a standard A.S.T.M. tensile bar with a ½-in. reduced section. Four bars are produced in one mold.

TABLE 1.—*Commercial Magnesium-base Alloys*

Alloy	Heat-treatment	Composition, Per Cent			Normal Grain Size, In. × 10^{-3}	Typical Tensile Properties		
		Al	Zn	Mn		Elongation, Per Cent	Yield Strength, 1000 Lb. per Sq. In.	Tensile Strength, 1000 Lb. per Sq. In.
C-HTA......	2 hr. 500°–770°F. + 16 hr. 770°F. + air cool + 10 hr. 425°F.	9	2	0.2	4	2	23	40
H-HT.......	2 hr. 500°–730°F. + 10 hr. 730°F. + air cool	6	3	0.3	4	12	14	40
H-HTA......	H-HT + 16 hr. 350°F.	6	3	0.3	4	5	19	40

Variations of grain size were produced by varying the thermal treatment of the melt. As will be briefly discussed later, this has a pronounced effect on the grain size of a magnesium-alloy casting. Table 2 indicates the direction of this effect and illustrates the manner by which a range of grain sizes was obtained.

Tension Tests

The results of the tensile tests are listed in Table 4. Each result is the average of from 12 to 70 bars. Jeffries and Archer,[6] in 1922, suggested that with less than 1000 grains per cross section the number of grains per cross section rather than absolute grain size is the controlling factor, while with an excess of about 1000 grains per cross section the absolute grain size becomes important. Recently, Pell-Walpole[7] has shown that these ideas are correct for tin and tin alloys. He shows a linear relation between the logarithm of the number of grains per cross section and the tensile strength. His samples were all rather coarse grained.

The data of Table 4 are plotted against the logarithm of the reciprocal of the square of the average grain diameter in Fig. 1. A linear relation is found for each of the three alloys. Since $\left(\frac{1}{D^2}\right)$ is roughly proportional to the number of grains per cross section, a relation between this and tensile strength is strongly indicated. However, all the results for Table 4 were obtained on test bars of constant cross section. Therefore, new test bars of alloy C-HTA were prepared having a constant grain size but varying in cross-sectional area. The results are listed in Table 5. It is obvious that,

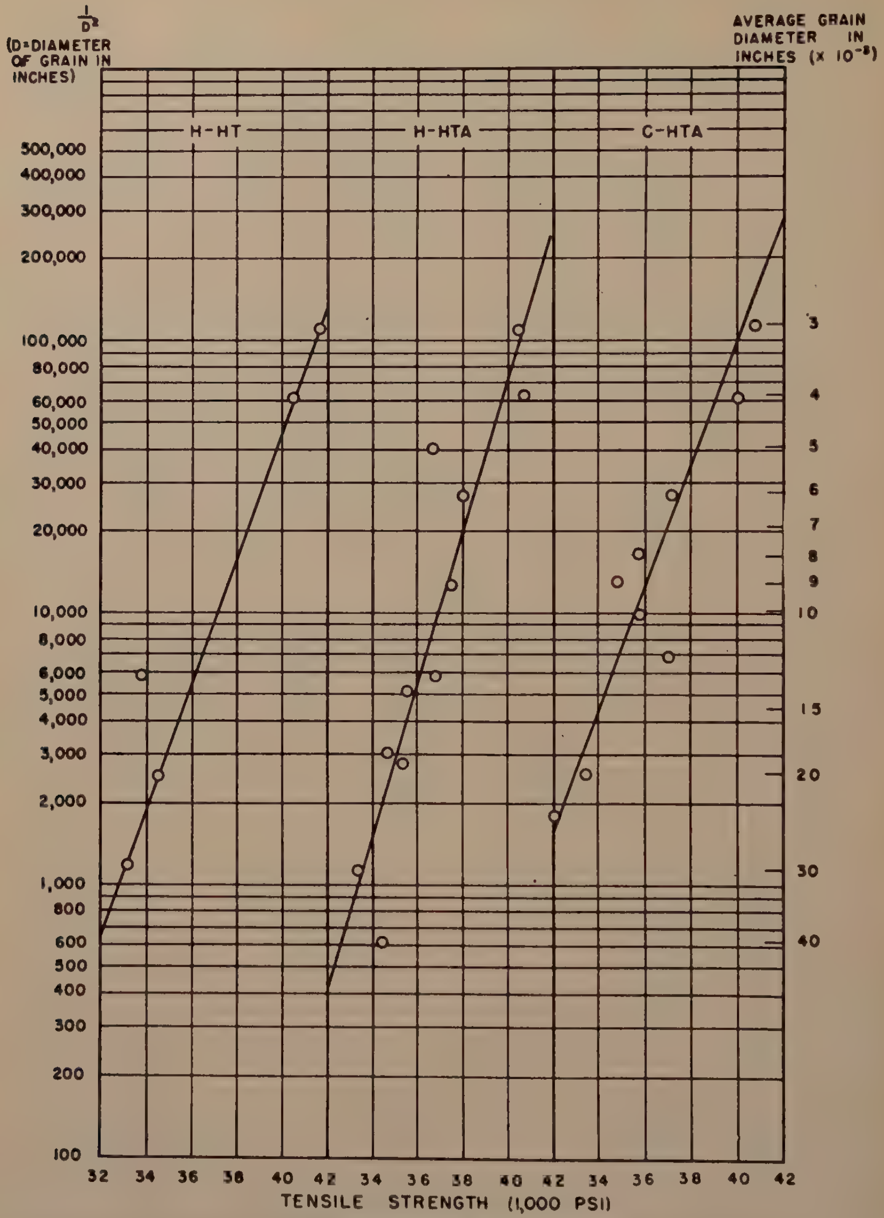

FIG. 1.—DATA OF TABLE 4 PLOTTED AGAINST LOGARITHM OF RECIPROCAL OF SQUARE OF AVERAGE GRAIN DIAMETER.

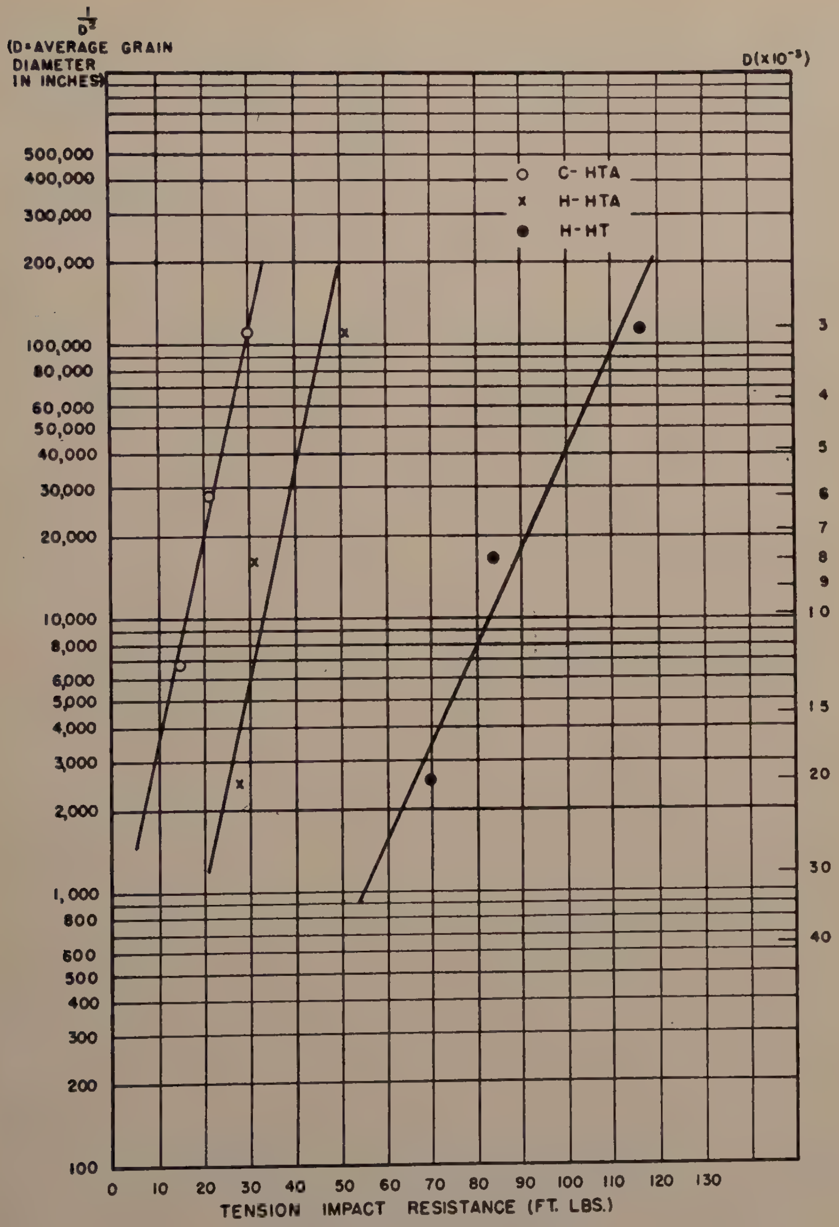

FIG. 2.—TENSILE IMPACT RESULTS.

within testing error, a decreasing number of grains per cross section has no effect on the tensile properties within the range of grain sizes investigated. Hence, the absolute grain diameter is the controlling factor.

The tensile impact results are given in Fig. 2. These were determined with a standard Riehle machine on bars machined to 0.375-in. reduced section from the cast test bars. There is a taper of 0.003 to 0.005 in. from the shoulder to the center of the reduced section, in order to prevent any shoulder breaks. A linear relation between this property also and log $\left(\frac{1}{D^2}\right)$ is obtained. This type of plot, because of its linear character, is convenient to use for interpolation and slight extrapolation of the data.

Under certain foundry conditions microporosity exists in magnesium alloys. The combined effect of porosity and coarse grain therefore is of engineering importance. The effect of porosity on the mechanical properties of magnesium alloys with a grain size of 4 has been reported.[8] Using metal with the larger grain size of 12, the results are as given in Fig. 3. The lines are taken from the previous work, therefore representing metal with a grain size of 4. The experimental points are the new determinations on coarser-grained material. The experimental points coincide with the lines within the experimental error. This study, therefore, indicates that the effects of grain size and porosity are not additive, within the range of commercial practice. In comparing Fig. 3 and Fig. 1, it must be remembered that the radiograph cannot detect the first amounts of porosity. Thus, at a $1/V$ value of 200, there is enough porosity already present to lower the strength to 35,000 lb. per sq. in. There is some indication in Fig. 3 that the effect of grain size becomes increasingly important as the porosity decreases.

Fatigue Properties

The fatigue strength of the three alloys was determined with polished samples on a standard R. R. Moore rotating-beam type of machine. The measurements were carried to 100,000,000 cycles, the value at this number being taken as the endurance limit. The effect of a notch was also studied, by using a circular notch with radius and depth equal to one tenth the root diameter. This results in a stress concentration of 2.0 at the root of the notch. Results are reported in terms of notch efficiency, which is the ratio of the endurance limit of the notched bar to that of the plain bar.

The fatigue test bars were prepared in the same way as were the tension bars. The same mold pattern was used, and the fatigue bars were machined from the cast test bars. The variation in grain size was obtained in the same manner as previously described.

The values for the endurance limits are plotted in Fig. 4. Once more, a linear relation is obtained between the property value and log $\left(\frac{1}{D^2}\right)$. Although the results for H-HT are quite scattered, for an unknown reason, the results for H-HTA and C-HTA are quite consistent and lie on the same curve within the limits of error.

Factors Affecting Grain Size

In view of the property decrease associated with increasing grain size, it becomes of interest to examine the factors that may influence the final grain size of a sand casting. While it is beyond the scope of the present paper to discuss fully each of the variables, a short discussion is given. Future publications will cover some of the more important factors in detail.

The factors that can affect the final grain size of a magnesium-alloy sand casting are the pouring temperature, sand condition, type of mold, alloy composition, thermal history of the melt, and subsequent heat-treatment. Of these, the first three are of

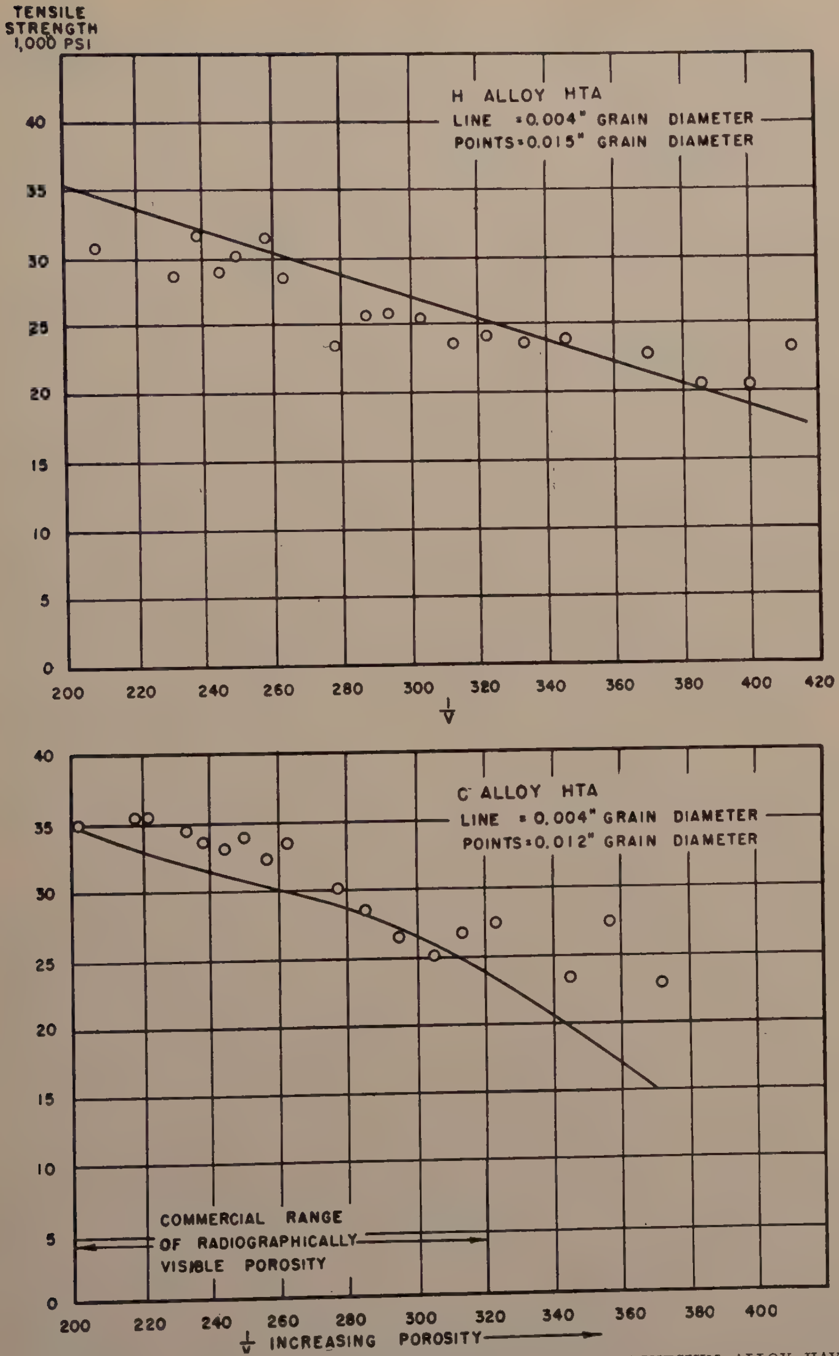

FIG. 3.—EFFECT OF POROSITY ON MECHANICAL PROPERTIES OF MAGNESIUM ALLOY HAVING A GRAIN SIZE OF 12.

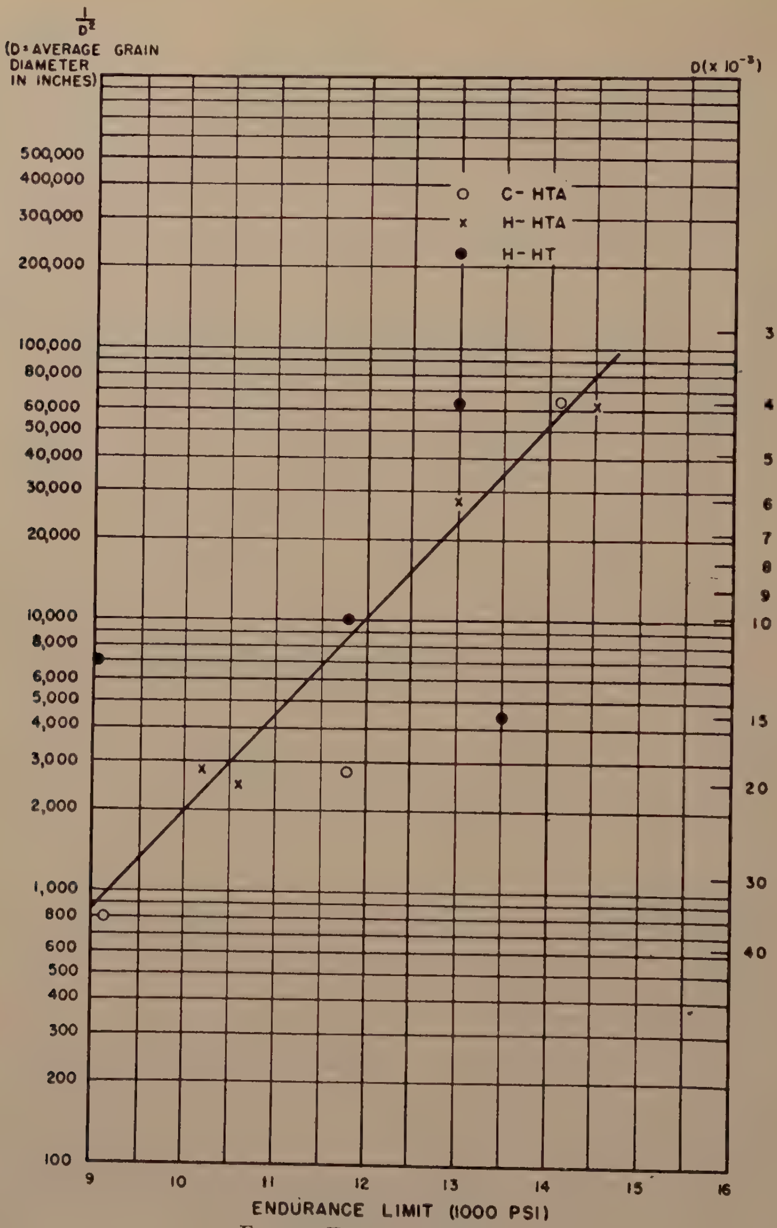

FIG. 4.—ENDURANCE LIMITS.

minor importance. Each of the other three is discussed briefly, being limited to the alloys for which property data were presented.

Composition

When pure magnesium freezes, large columnar crystals are formed, each extending to the center of the casting. The addition of manganese up to 5 per cent does not change the columnar type of formation. The addition of even a small amount of either aluminum or zinc has the effect of producing a casting with relatively small equiaxed grains. The grain-refinement effect of these elements becomes more pronounced as more of each is added, at least within the commercial range of composition. In the range of 6 to 10 per cent Al and 1 to 3 per cent Zn, the effect of aluminum is more pronounced than that of zinc. Thus, C alloy is finer grained than H alloy if no methods are used to refine either alloy. If superheating (see next column) is practiced, the alloys are about equally fine.

The grain size of C and H alloys may be further modified—increased or decreased—with certain other elements, which, however, are not normally used. Principal among the coarsening agents are beryllium, chromium and titanium. Small amounts of these will change the grain size from an average diameter of 0.004 in. to about 0.020 in. The opposite effect is obtained through the addition of zirconium. The refining effect of this element is especially evident when added to large-grained C + Be. Thus, C alloy + 0.001 per cent Be + 0.2 per cent Zr has a grain size of 0.007 in., obtained without superheating.

The time in the melting cycle at which an element is added is sometimes important. Thus, C + 0.02 per cent Ca when properly refined has a grain size of 0.004 in. However, if the calcium is added within 5 min. of the pouring time, the grain size becomes 0.01 to 0.02 inch.

Thermal History of the Melt

As is true with many other metals, the grain size of a casting of magnesium alloy is sensitive to the amount of overheating the melt receives. In the C or H alloys, the effect of superheating 500° to 700°F. above the liquidus is to produce a finer grained casting than would have been produced by omitting such a superheating treatment.

TABLE 2.—*Effect of Temperature of Melt on Properties of C-HT*

Poured at 1400°F. Liquidus, 1105°F.

Temperature, Deg. F.	Time at Temperature, Min.	Time at 1400°F. before Pouring, Min.	Average Grain Diameter, In.
1240	15	0	0.008
	30	0	0.010
	60	0	0.015
1400	15	0	0.010
	30	0	0.010
	60	0	0.010
1500	15	0	0.008
1600	15	0	0.004
1700	15	0	0.004
1700	15	15	0.004
1700	15	30	0.006
1700	15	120	0.010

Table 2 lists the effects of different temperature treatments on the grain size of C alloy. In these incomplete experiments, the pouring temperature, mold, and sand were held constant. It is evident that superheating has a definite effect on the grain size of C alloy. Similar results are obtained with H alloy. The beneficial effect of superheating does not persist if the metal is cooled and then held for a long period at a lower temperature.

The effects of superheating persist somewhat upon remelting; that is, C alloy superheated 15 min. at 1700°F. and poured, then remelted and poured at 1400°F., will tend to have fine grain. As would be indicated by Table 2, however, repetition of this process, corresponding to longer holding at 1400°F., soon leads to a grain coarsening.

It is not within the scope of this paper to discuss theories of superheating that have been proposed. A rather extensive discussion is given by Achenback, Nipper, and Piwowarski.[1]

Heat-treatment

The grain size of a magnesium-alloy casting obtained as a result of the molten metal treatment is often modified by heat-treatment. This takes the form of a grain growth, either gradual and slight or rapid and extensive. The first type is illustrated in Table 3.

TABLE 3.—*Grain Growth in C Alloy*

TIME AT 770°F., HR.	AVERAGE GRAIN DIAMETER, IN.
0	0.004
18	0.005
36	0.006
54	0.006
72	0.008

For this experiment, C alloy was superheated 30 min. at 1700°F. and poured in sand at 1400°F. It is evident that a long time at the temperature of heat-treatment may lead to some enlargement of the grain diameter.

TABLE 4.—*Effect of Grain Size on Tensile Properties*

Specimen Diameter, 0.5 Inch

Average Grain Diameter, In. × 10^{-3}	C-HTA			H-HT			H-HTA		
	Elongation, Per Cent	1000 Lb. per Sq. In.		Elongation, Per Cent	1000 Lb. per Sq. In.		Elongation, Per Cent	1000 Lb. per Sq. In.	
		Y.S.	T.S.		Y.S.	T.S.		Y.S.	T.S.
3	1.5	25.1	40.9	14.7	14.0	41.8	4.9	22.1	40.4
4	1.3	25.3	40.0	14.4	14.2	40.5	5.8	21.1	40.9
5							2.6	18.8	36.7
6	1.6	24.0	37.2				5.2	18.5	38.0
8	1.9	23.7	35.8						
9	0.7	25.1	34.8				4.2	16.8	37.5
10	1.4	22.0	35.7						
13	2.6	23.4	37.2	9.2	12.2	33.9	4.6	20.2	36.8
14							4.6	17.0	35.7
18							4.0	16.8	34.7
19							4.5	17.2	35.5
20	0.9	22.8	33.5	9.8	11.7	34.5			
24	0.9	21.9	32.0						
30				9.4	12.8	33.1	3.6	19.1	33.3
40							4.6	20.2	34.6

When certain quite critical, but controllable, conditions are fulfilled, C alloy and other alloys of similar aluminum content will exhibit a very extensive grain coarsening during heat-treatment. This type of coarse grain is very different from any that occurs during casting. In the casting process grain sizes of over 0.050 in. are seldom encountered. Germinated[2] grains, on the other hand, may be from 0.125 to as much as ¾ in. in diameter. These large grains lower the tensile strength of C-HTA alloy to 15,000 to 20,000 lb. per sq. inch.

The main factors of importance for producing germinated grains are alloy composition, chill practice, stress, and heat-treatment. The phenomenon can be kept under control by proper attention to mold design and careful control of heat-treatment practice. It should be emphasized that this runaway type of grain growth is of an entirely different order of magnitude from the coarse grains sometimes produced during the casting process. Its occurrence is not usual and well-known control methods can eliminate it.

DISCUSSION OF RESULTS

Table 6 presents in summarized form the results reported. All data except those for one alloy are graphical averages obtained by plotting original data as in Figs.

1, 2, and 4. The exceptions are the data for the fatigue strength of H-HT. These experimental values are entered in Table 6 because of their excessive scattering.

TABLE 5.—*Effect of Varying Cross Section on Tensile Properties of C-HTA*
Average Grain Diameter, 0.005 Inch

Diameter of Bar, In.	Area, In.	Number Grains per Cross Section	Elongation, Per Cent	Y.S. 1000 Lb. per Sq. In.	T.S. 1000 Lb. per Sq. In.
0.437	0.150	6,000	1.5	25.6	41.6
0.375	0.110	4,400	1.0	26.7	41.4
0.310	0.076	3,000	1.5	25.3	41.7
0.250	0.050	2,000	2.0	27.3	41.4
0.188	0.028	1,850	1.3	27.8	40.3
0.350 × 0.188	0.067	2,700	1.7	24.5	40.2

The fatigue results given in Table 6 do not correspond in every way with published typical values of these alloys.[9] The values given here are for a small number of batches of metal, and are measured at 100,000,000 cycles. Typical values are determined on a large number of batches of metal and are measured at 500,000,000 cycles. The values of Table 6 and published typical values are in agreement within the errors of fatigue testing.

The results reported are on separately cast test bars in which all variables except grain size are held constant. Since the ultimate value of such data is an understanding of the effect of grain size on the serviceability of castings, it is important to judge the relative importance of grain size compared with other possible defects. One such comparison was made with the data shown in Fig. 3, where the combined

TABLE 6.—*Effect of Grain Size on Properties of Magnesium Alloys*
Stress Concentration, 2.0

Alloy	H-HT			H-HTA			C-HTA		
Grain Size	4	10	20	4	10	20	4	10	20
Tension properties:									
Elongation, per cent	14.4	12.2	9.4	4.4	4.4	4.4	1.4	1.4	1.4
Yield strength, 1000 lb. per sq. in.	13.8	12.6	11.4	21.2	18.6	16.6	25.0	23.5	22.5
Tensile strength, 1000 lb. per sq. in.	40.8	37.2	33.8	39.8	37.0	34.0	39.4	35.6	32.8
Impact, ft-lb	105	83	66	43	33	27	26	16	8
Fatigue properties:									
10^6 cycles 1000 lb. per sq. in.	20.5	17.9		21.2	19.1	17.5	21.2	19.1	17.5
10^7 cycles 1000 lb. per sq. in.	15.0	13.5		15.8	13.7	12.2	15.8	13.7	12.2
10^8 cycles 1000 lb. per sq. in.	13.0	11.8		14.2	12.0	10.3	14.2	12.0	10.3
Notch efficiency[a]				0.65	0.68	0.74	0.65	0.68	0.74

[a] $\frac{\text{Notched Value}}{\text{Unnotched Value}}$.

TABLE 7.—*Tensile and Metallographic Data on C-HTA Machined from a Series of Production Castings*

Bar No.	Tensile Strength, Lb. per Sq. In.	Compound[5]	Average Grain Size, In.	Size Large Grain, In.	Porosity		
					Micro	X-ray	Fracture
1	29,950	4–5	15	30	0		
2	31,350	4	9	15	0		
3	29,750	3–4	10	20	0		
4	24,600	4–5	9	15	0		Yes
5	21,350	4	15	30	0		Yes
6	29,600	3–4	9	50	0	No	Yes
7	25,000	3–4	15		0	No	Yes
8	33,800	2–3	15		0	No	No
9	20,800	2–3	15		0	No	Yes
10	19,750	4–5	5	15	0	Yes	Yes
11	37,000	2	15		0	No	No

effect of porosity and grain size is presented. For these tests the porosity completely overshadows the grain size, so that it is impossible to detect any effect of grain size when very much porosity is present.

Table 7 is of bars cut from two production castings. The grain size, compound rating,[5] microscopic porosity,[5] radiographic porosity, and the porosity visible at the fracture are all given. There are two bars in this table, Nos. 8 and 11, that have low strength due solely to large grain size. The strength values reported agree well with the curve for C-HTA in Fig. 1. Values for the other bars are below the curve in Fig. 1, and in each case some factor other than grain size is present. The evidence of Table 7 is that, although grain size has a deleterious effect on mechanical properties, the effect is small compared with that of other variables; e.g., porosity.

Because it is possible to superheat magnesium-base alloys, the grain size of commercial castings can be kept well under control. The average size is about 0.006 in., and it is rare to find any larger than 0.030 in. Comparing this range with the data on properties, it is seen that the magnitude of the property effect is small. Thus, while grain size does have a positive effect on mechanical properties and should, therefore, be carefully controlled, such control is available, and emphasis should be placed on other variables that adversely affect mechanical properties.

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DISCUSSION

(*M. A. Hunter presiding*)

R. E. WICK.*—The authors mention that sand condition is of minor importance in the control of grain size. Sand is the medium through which heat is dissipated. The physical condition of the sand directly affects the rate of heat flow. The rate of heat flow in turn affects the rate of solidification. Grain size is partially dependent upon the rate of solidification.

At Battelle Memorial Institute, work has been done on the use of grain refiners to be substituted for superheating. Have the authors any further data on the use of grain refiners?

R. S. BUSK and C. W. PHILLIPS (authors' reply).—Grain size is dependent upon the rate of solidification, and, more important, upon the temperature gradients within the solidifying metal. It is true that sand condition will affect both of these factors. However, a property of magnesium is its relative insensitiveness to these two things, so that in comparison with such factors as superheating and composition the effect of sand condition is minor.

The subject of the grain refinement of magnesium alloys has been extensively studied in the past several years, both in our laboratory and elsewhere. However, the subject is broad, making a lengthy discussion of it unjustified here. We may say simply that many methods, including those published by the Battelle workers, have been found which refine the grain to the same degree that superheating does.

MEMBER.—I wish Mr. Phillips would enlarge on the question as to just how he tied in the completion of solution of heat-treatment with the mechanical properties that were obtained upon the graph.

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* Laboratory Technician, The Hydro-Blast Corporation, Chicago, Illinois.

C. W. Phillips.—Each sample is examined under the microscope for complete solution.

Member.—Each one of the samples was heat-treated long enough to have them in complete solution?

C. W. Phillips.—That is correct.

R. T. Wood.*—How much did the grain size increase during heat-treatment?

C. W. Phillips.—From 0.003 to 0.004 inch.

R. T. Wood.—We have never been able to convince ourselves that such an enlargement takes place, mainly because of the great difficulty we have in estimating the grain size of as-cast material. What was your method of estimating the grain size of as-cast material?

C. W. Phillips.—I believe Mr. Hess could help us with that. What is the method you use for the as-cast grain size?

J. B. Hess.†—Although it is rather difficult to measure the grain size of as-cast magnesium alloys, it can be done with a little experience. The difficulty is in the fact that the beta-phase network, in addition to outlining the grain boundaries, frequently extends into the interior of dendritic spaces, and thus provides the temptation of measuring such nearly surrounded dendritic lobes as separate grains. However, when the samples are etched about ten seconds in the acetic-picral etchant, those portions of the true grain boundary that lie between the individual beta particles in the beta network are clearly revealed, and the actual grain size can be traced out.

Member.—I have heard conflicting reports of the effectiveness of the zirconium as a grain refiner. How is it added? Also chromium?

C. W. Phillips.—Zirconium usually is added as zirconium chloride flux, which we obtain from the Titanium Alloy Manufacturing Co. The amount gotten in, of course, is small; nevertheless it is there. A pronounced effect of zirconium is on an alloy or C plus beryllium, which ordinarily is coarse grained. You remember I mentioned that beryllium is a coarsener. Zirconium added to berylium will again refine the grain. The exact nature of the mechanism is not known.

Member.—Do you always obtain the grain-refining effect? People tell us that it is not obtained in all alloys.

C. W. Phillips.—That is true. On certain alloys you do not get it, but the example listed in the paper was C alloy plus beryllium.

Member.—A considerable range in the tensile strength is shown—about 25 per cent. Is there any reference to hardened specimens on the surface cores?

C. W. Phillips.—There are no references concerning the hardness.

Member.—Is there any reason why there would not be a similar relation?

C. W. Phillips.—No, none whatever.

R. S. Busk.—I might add one thing. Zirconium addition always results in refinement, if it is successfully introduced.

Member.—How much zirconium do you want to get in? What does your analysis on zirconium content show?

R. S. Busk.—On the order of 0.05 per cent in the presence of aluminum.

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Water Quenching of Some Typical Magnesium Casting Alloys

By R S. Busk* and R. E. Anderson*

(New York Meeting, February 1945)

The mechanical properties of many nonferrous alloys can be modified by heat-treatment. This is almost always effected by controlling the amount of alloy in solid solution and the amount and distribution of second-phase material. The latter often is accomplished through precipitation or age-hardening treatments. The procedure is to solution-heat-treat the metal to provide a supersaturated solid solution and then cause precipitation of the dissolved material at some temperature below the solvus for the alloy.

The generally used magnesium sand-casting alloys are based on the ternary alloy system Mg-Al-Zn. Solid diffusion reactions in the system are slow enough so that a substantially completely supersaturated solution is maintained even though the metal is relatively slowly cooled from heat-treating temperatures. Consequently, it is general practice to air-cool magnesium-alloy castings from the heat-treatment temperature prior to aging at an elevated temperature. Since it is necessary with many other alloys to cool quite rapidly before aging if optimum benefit from the aging is to be obtained, this study was undertaken to determine the effects of quenching on magnesium alloys.

The alloys used are shown in Table 1, being selected as typical of the presently used magnesium alloys.

COOLING RATES

Since quenching is a means of rapidly extracting heat, there are two factors of interest in its study: (1) the rates of cooling that can be obtained and (2) the effect of various rates on the as-cooled as well as subsequently aged metal.

The cooling rates were measured by drilling a hole 1⁄16 in. in diameter longitudinally in the center of a cylinder 3⁄4 in. in diameter and 3 in. long. The drilling was stopped to place the end of the hole at the center of the long axis of the cylinder. An iron-constantan thermocouple was inserted in this hole and wedged in place.

The temperature drop during rapid quenching was recorded by a specially built General Electric potentiometer recorder capable of measuring a 500°F. temperature drop in 1⁄10 sec. For the slower cooling rates in air or oil, the temperature drop was measured by a Leeds and Northrup potentiometer recorder with the chart speed increased to one inch per minute. The cylinder was heated to the desired temperature, quenched as desired, and the temperature-time curve recorded. The cooling rates in still air, in oil at 350°F., in water at 180°F. and in a cold, high-pressure water spray were determined in this manner.

The results of this study are presented in Fig. 1. There is a great difference between water quenching and either air or oil quenching. There is little difference between the hot water quench and the cold water spray. Cooling rates were also

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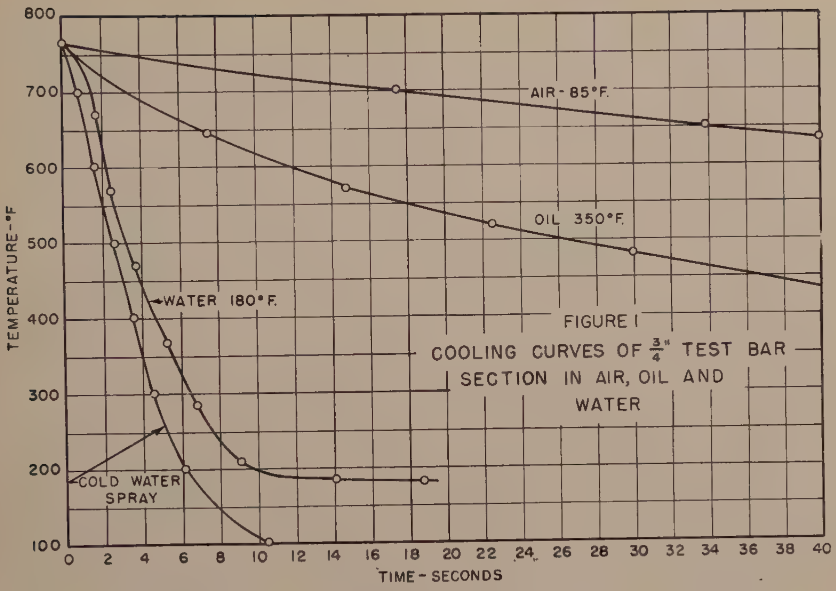

Fig. 1.—Cooling curves of ¾-inch test-bar section in air, oil and water.

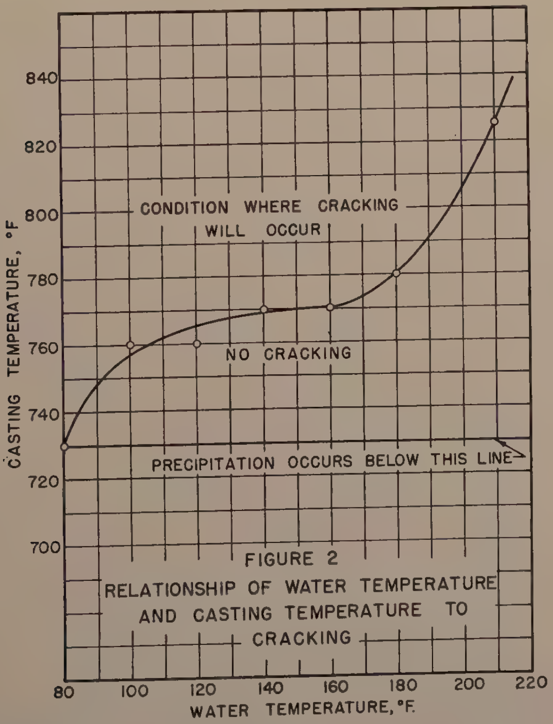

Fig. 2.—Relationship of water temperature and casting temperature to cracking.

measured in a 25 per cent brine-ice mixture at 0°F. and in a dry-ice iso-amyl ether mixture at minus 94°F. The cooling rates in these mixtures were no faster than in the water spray.

It is possible to combine the data of Fig. 1 with the thermal properties of the metal and arrive at a figure for the heat-transfer coefficient (h_T).[1] When this is done, h_T for the 180°F. water quench is found to be 1200, while that for air is about 13 B.t.u. per deg. F. per sq. ft. per hr. Knowing the heat-transfer coefficient for any given quenching procedure, it is possible to calculate the cooling rate for any section size. When this is done for quenching into water at 180°F. it is found that a section 0.1 in. thick will cool from 770° to 370°F. in ½ second.

Induced Stresses

When a complicated casting is chilled suddenly, different cooling rates are produced in the various sections. This gives rise to stresses, due to differential contraction, which may result in residual stresses, warping, or cracks.

Extensive relaxation tests have been made in this laboratory with cast to shape specimens of C and H alloys. Each specimen, 3⁄16 in. thick, 6 in. long, and varying in width from ½ to ⅛ in., was loaded in a jig as a uniformly stressed cantilever beam, and heated in a controlled furnace. The test is essentially a constant deformation type of creep test and the decrement of load to produce that deformation after a given heat-treating cycle was taken as a measure of the amount of stress relieved during the cycle. Variations in initial stress, time, and temperature were studied. These studies show that there is rapid relief of stress during precipitation treatments. Thus in the heat-treated C alloy, 50 per cent of the stress is relieved in 1.5 hr. at 350°F. while all the stress is relieved in 10 hr. at 350°F. Heat-treated H alloy requires somewhat longer at 350°F., but in 2½ hr. 50 per cent of the stress is relieved while in 24 hr. all stress is relieved. At 500°F. either alloy is completely stress-relieved in one hour. These figures are independent of the absolute magnitude of the stress. Therefore, it is safe to state that heat-treated, quenched, and aged magnesium castings will have very small if any residual stresses.

All the dimensions of several complicated aircraft-engine castings have been carefully measured before treatment. After quenching, remeasurement has not revealed any sign of dimensional change. In these cases, the first measurements were on heat-treated and air-cooled castings, which were then merely raised to the proper temperature and quenched, eliminating changes due to solution heat-treatment. Thus, warpage as a result of quenching is not apparently a significant problem with magnesium-alloy castings.

Cracking due to quenching will occur if the induced stresses exceed the ultimate strength. This can occur only if the metal is not able to relieve the stress by plastic flow. The stresses at room temperature are far below the strength of the metal, and at moderately high temperatures the metal is quite ductile. Therefore, within the limitation of usual casting design, any cracking can occur only in the hot-short range, where the strength is low and the ductility zero. That this is true is indicated by the fracture appearance of a quenching crack that exactly follows the grain boundaries.

The temperature above which each of the alloys is brittle is therefore of interest. This was found by supporting a test bar as a cantilever beam, raising to the desired temperature and striking the end with a hammer. If ductile, the bar bends; if brittle, it breaks with no bending and with an intergranular fracture. In this way the brittle temperatures were determined to be 670°F. for C and H alloys, and 700°F. for R alloy. It is clear that if normally designed castings are quenched from below these temperatures, no cracking will occur but if quenched from above these temperatures there is danger of cracking. The result will depend on the magnitude of stress developed before the section is cooled below the brittle point.

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[1] References are at the end of the paper.

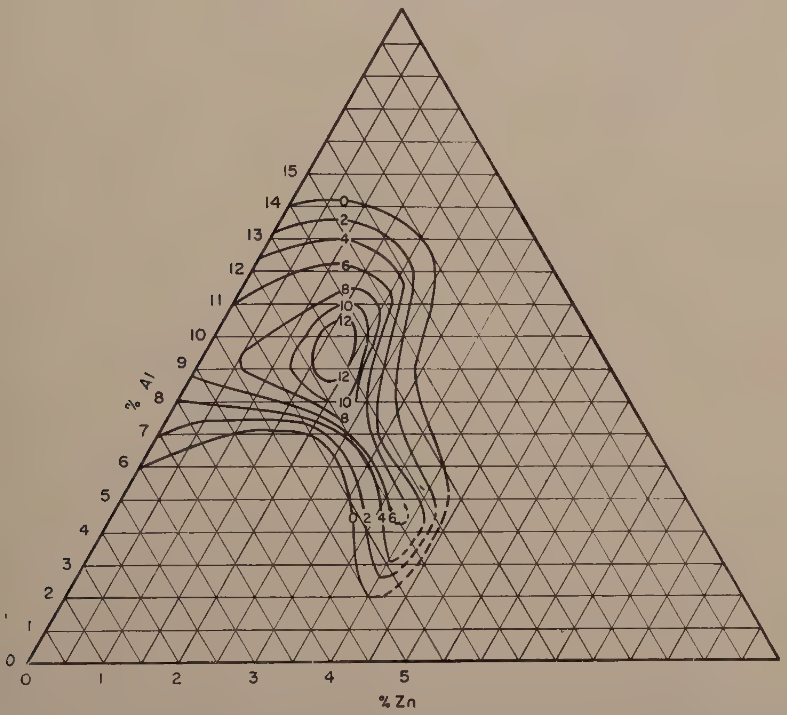

Fig. 3.—Improvement in tensile strength of aged test bars due to water quenching from solution heat-treatment temperatures.
Expressed in 1000 pounds per square inch.

Since the solvus for C alloy (700° to 725°F.) is above the brittle temperature, a series of experiments was run to determine the limits within which it is safe to quench. A special panel, 3 by 4 by ¼ in., was used. This had a saw cut about 1 in. long in the center of the 4-in. side parallel to the 3-in. side. The panel was heated to the desired temperature, then quenched so that a 4 by 1½ by ¼-in. section was below water, the side with the notch above water. This created very large stresses at the root of the notch and led to cracking when the quenching was severe enough. Quenching temperatures at 10°F. intervals and various water temperatures were tried. It was found that the higher the quenching temperature, the higher the water temperature had to be to prevent cracking. Fig. 2 gives the results. The experimental points indicate the lowest quenching temperature that will result in cracking at a given water temperature. Cracking will not occur at any point below the curve, but will occur at any point above the curve. The notched panel used is considered to develop higher stresses when quenched than any commercial casting; therefore the curve of Fig. 2 indicates the limit to be expected in practice; it is recommended that any point representing quenching conditions be 10° to 20°F. below this curve.

TENSILE DATA ON SEPARATELY CAST TEST BARS

Cast test bars conforming to American Society for Testing Materials specifications were used and tested without machining. The standard solution heat-treatments listed in Table 1 were applied to each alloy. Unless otherwise stated, "aging" refers to a treatment of 18 hr. at 350°F.

TABLE 1.—*Magnesium-alloy Compositions and Standard Solution Heat-Treatments*

Alloy	Composition, Per Cent			Heat-treatment
	Al	Zn	Mn	
C	9	2	0.2	2 hr. 500–770°F. + 18 hr. at 770°F.
H	6	3	0.2	2 hr. 500–730°F. + 10 hr. at 730°F.
R	9	0.7	0.2	2 hr. 500–780°F. + 18 hr. at 780°F.

The effect of cooling rate on the tensile properties is presented in Table 2. Considerable improvement is effected with C alloy, some with H and R alloys. There is a direct relation between the rate of cooling and the improvement of mechanical properties.

TABLE 2.—*Effect of Cooling Rate on Tensile Properties of Subsequently Aged C, H, and R Alloys*

Cooling Time from 770° to 370°F., Sec.[a]	C			H[a]			R		
	% E	Y.S.[b]	T.S.[b]	% E	Y.S.[b]	T.S.[b]	% E	Y.S.[b]	T.S.[b]
190	2.0	24.1	40.0	5.0	19.2	40.0	2.5	22.9	40.0
65	1.8	25.0	41.9	3.4	23.4	40.4	2.0	23.6	40.2
5.5	2.2	30.0	45.9	5.7	21.7	42.4	2.6	23.1	40.6
0.5	3.5	29.9	48.2	7.3	21.6	45.1	3.3	24.6	44.4

[a] H alloy cooled from 730° to 330°F. in indicated number of seconds.
[b] 1000 lb. per sq. inch.

A survey was made of the maximum improvement obtained by quenching many compositions within the magnesium-rich corner of the Mg-Al-Zn diagram. The alloys used had about 0.2 per cent Mn added. The results, expressed as the difference between the tensile strengths of air cooled and aged, and quenched and aged bars, are given in Fig. 3. The maximum improvement and the maximum properties are in the composition range of C alloy. There is an apparent discrepancy between Table 2 and Fig. 3. The data for Fig. 3 represent the maximum improvement experienced with each alloy on machined bars, while Table 2 represents averages of a large number of unmachined bars. The effect of machining is to raise the strength from 5 to 10 per cent.

TABLE 3.—*Effect of Quenching Conditions on Tensile Strength of Subsequently Aged C Alloy*

Quench to, Deg. F.	Quench from, Deg. F.								
	600	700	730	740	770	780	800	810	820
Tensile Strength, 1000 Lb. per Sq. In.									
80	43.8	45.8	49.3		44.5				
100		48.4	48.8		44.0				
120		46.8	47.1		43.9				
140		45.2	48.3		43.5				
160		45.8	47.1		44.2				
180		47.0[a]	46.5	43.9	45.9	45.8	46.8	45.1	35.6[b]
Yield Strength, 1000 Lb. per Sq. In.									
80	27.3	29.0	29.4		29.6				
100		29.1	29.0		30.0				
120		28.9	29.6		30.0				
140		29.1	30.0		29.4				
160		27.7	28.7		29.4				
180		29.9	27.7	27.5	30.0	29.7	29.4	28.3	29.4
Percentage of Elongation									
80	2.1	1.5	2.5		1.3				
100		2.2	2.6		2.0				
120		1.6	1.7		1.9				
140		1.5	2.0		1.9				
160		2.2	2.0		1.9				
180		2.4	1.2	2.3	2.2	2.3	2.2	2.1	1.0

[a] 715°F.
[b] All bars cracked.

Aside from the possibility of cracking, as discussed previously, it is of interest to know whether there are optimum quenching conditions. Accordingly a series of

C-alloy bars were quenched under different conditions, as shown in Table 3, where the results are given. There is little difference over the range of temperatures tried. The low results on quenching from 820°F. are caused by cracking of the test bars. The high results on quenching from 730°F. to 100° and to 80°F, are probably due to faster cooling. Although one would expect this to be apparent on quenching from 770° to 80°F., the lower results are probably due to some cracking. Although no cracks were observed, these conditions always cracked the panel (see Fig. 2) and small cracks may have been present. This is further borne out by the low percentage of elongation. The lower results on quenching from 700° to 80°F. and from 600° to 80°F. are due to some high-temperature precipitation that occurs at these temperatures, since the solvus for C alloy is between 700° and 725°F. The data of Table 3 indicate that quenching should be from as low a temperature as possible consistent with the curve of Fig. 2.

TABLE 4.—*Effect of Time and Temperature of Aging on Properties of Alloys Quenched from Heat-treating Temperature to 180°F.*

Alloys	Deg. F.	5 Hours			15 Hours			25 Hours		
		% E	Y.S.[a]	T.S.[a]	% E	Y.S.[a]	T.S.[a]	% E	Y.S.[a]	T.S.[a]
C	300	8.3	22.3	42.8	3.7	27.6	45.5	2.5	28.3	45.0
	350	2.3	27.9	43.8	2.2	30.0	45.9	1.7	28.7	43.7
	400	2.1	29.4	43.4	1.7	29.6	43.1	2.0	27.2	41.6
	450	2.6	24.7	41.5	2.5	24.1	40.5	2.8	22.9	40.0
	500	3.3	24.1	39.3	3.2	22.9	39.1	3.3	22.2	39.0
H	300	14.4	15.7	41.2	12.5	17.6	42.6	11.5	18.4	43.2
	350	7.0	19.3	40.5	5.7	21.7	42.4	5.4	21.3	40.2
	400	7.0	20.9	40.5	5.7	21.6	40.7	5.4	20.4	40.2
	450	7.4	18.1	38.7	6.3	18.7	37.8	5.8	18.7	37.5
	500	7.4	17.8	38.0	6.3	16.8	36.0	5.8	16.6	34.7
R	300	12.8	14.8	41.1	11.7	16.0	41.1	10.3	17.3	41.8
	350	4.7	23.0	40.7	2.6	23.1	40.6	3.2	24.5	40.1
	400	4.7	21.9	40.7	3.5	23.2	40.1	3.2	23.4	40.1
	450	5.4	21.2	39.3	4.4	19.5	38.0	4.7	19.1	37.5
	500	5.4	20.2	36.9	4.4	18.9	36.5	4.7	19.0	37.0

[a] 1000 lb. per sq. inch.

Table 4 presents the effect of various times and temperatures of aging on the tensile properties of the alloys. The effects of underaging, critically aging and overaging are clearly demonstrated. The maximum yield strength for each alloy is attained at about 15 hr. at 350°F. An excellent combination of elongation, yield and tensile strength is attained in 5 hr. at 300°F. Such a combination of properties might be useful in many room-temperature applications, but since the precipitation is not complete, the alloy with this treatment is not entirely dimensionally stable at temperatures above 200°F. At room temperature, precipitation is slow enough so that for practical purposes the alloy is stable.

MICROSTRUCTURES

Selected microstructures are shown in Figs. 4, 5 and 6. Fig. 4 presents the effect of rate of cooling on the as-quenched and on the aged C-alloy structure. The grain boundaries are quite kinked and many patches of a pearlite type of precipitation are visible after air cooling. The oil quench eliminates the kinks in the grain boundaries and no pearlite patches can be seen. However, the boundaries are very broad and lumpy and etching is quite rapid, indicating some precipitation in the boundaries. After water quenching, all grain boundaries are straight, there is very little broadening, and etching is quite slow. Probably very little precipitation has occurred.

There are two distinct types of precipitation visible in the aged structure. One, the discontinuous type,[2] is at the grain boundaries, and resembles pearlite in appearance. The second is the continuous type, occurring within the grains and oriented in each grain. The principal difference observed as the rate of cooling is increased is a change in the ratio of the two types of precipitation. As the rate increases, the continuous type becomes more dominant. The relation, however, is not linear, and as the rate of cooling increases the rate of change of the ratio becomes smaller.

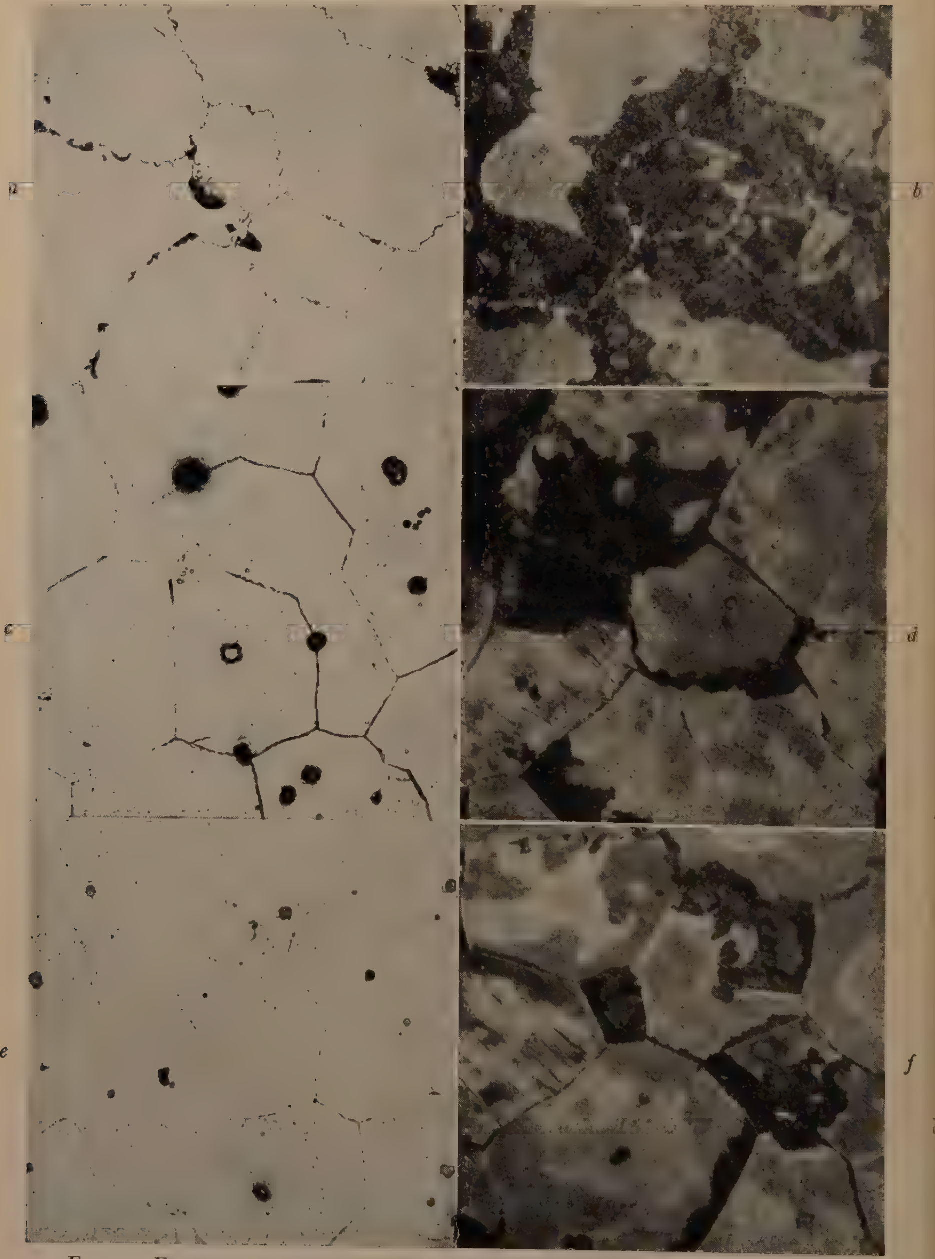

FIG. 4.—EFFECT OF RATE OF COOLING ON MICROSTRUCTURE OF C ALLOY. × 250.
a. Air cooled.
b. Air cooled + 18 hours at 350°F.
c. Oil quenched to 350°F.
d. Oil quenched to 350°F. + 18 hours at 350°F.
e. Hot-water quenched.
f. Hot-water quenched + 18 hours at 350°F.

With the fastest rates of cooling so far obtainable, there is about 5 to 10 per cent discontinuous type of precipitate in C alloy.

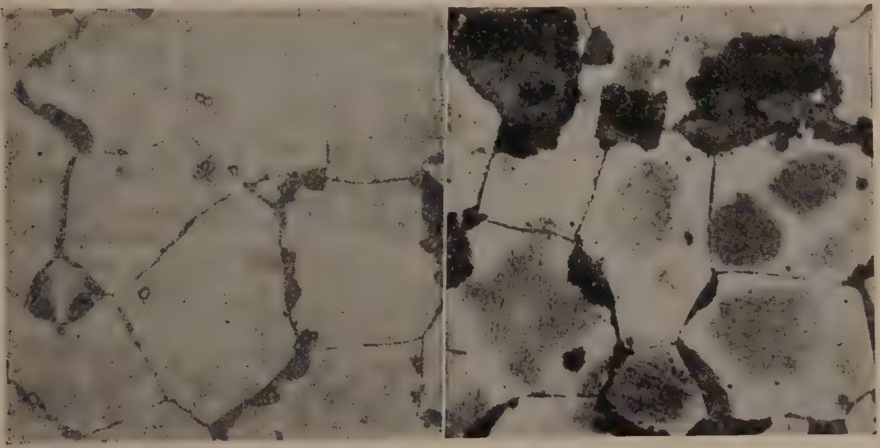

FIG. 5.—EFFECT OF HOT-WATER QUENCHING ON AGED MICROSTRUCTURES.
a. H alloy. *b.* R alloy.

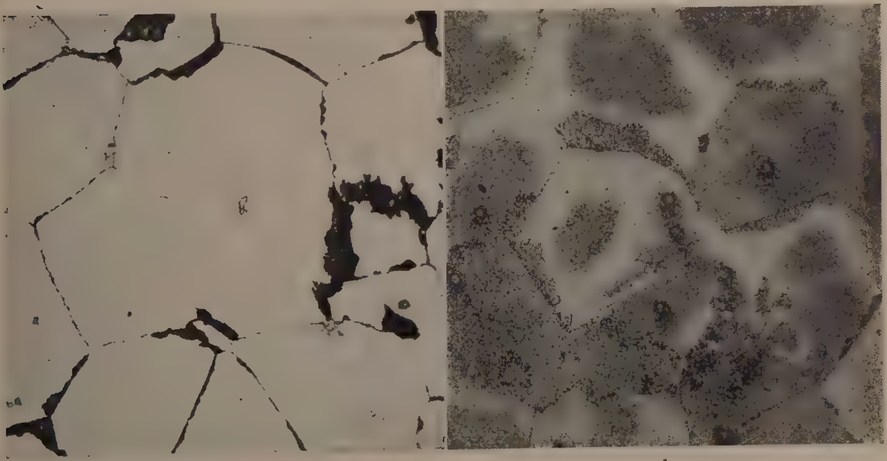

FIG. 6.—EFFECT OF TEMPERATURE OF AGING UPON MICROSTRUCTURE OF HOT-WATER QUENCHED C ALLOY. × 250.
a. 15 hours at 300°F. *b.* 4 hours at 500°F.

Fractures show that the crack produced by tension tends to follow through the discontinuous type of precipitation. As the amount of this type of precipitate decreases, it becomes increasingly difficult to find a continuous path through it and part of the fracture is then through the continuous type. This may be the explanation for the increase in tensile values as the rate of cooling is increased.

Fig. 5 illustrates the quenched and aged structures of the two other alloys. There is a high ratio of continuous to discontinuous types of precipitate in both. However, there is not as much of either type as in the C alloy. The continuous precipitation in H and R alloys appears somewhat coarser than in C alloy, which may be the reason for the lower strength of the former.

Fig. 6 shows the effect of temperature of aging on the microstructure of quenched C alloy. At 300°F. there is almost as much pearlite present as at 350°F. but it is very much finer. There is very faint evidence of the continuous type of precipitation within the grains. At 500°F. the entire structure is coarse, exhibiting a typical overaged appearance. It is difficult to distinguish between the two types of precipitate.

Effect of Defects

The results given have all been on separately cast test bars with fine grain size, good solution, and no porosity. Since the ideal is seldom completely attained in complicated castings, it is necessary to examine the effects of each defect on the quenched and aged properties. C alloy is chosen for this because it is most improved by the quenching.

Table 5.—*Effect of Grain Size and Compound Rating on Effectiveness of Quenching C Alloy from 770°F. to 180°F.*

Grain Size, In., $\times 10^{-3}$	Compound[a]	Quenched			Air-cooled		
		%E	Y.S.[b]	T.S.[b]	%E	Y.S.[b]	T.S.[b]
4	0	2.2	29.0	47.5	1.0	27.0	40.0
	1	2.2	29.0	47.5	1.0	27.0	40.0
	4	1.7	28.5	45.0	1.0	27.0	40.0
	6	1.4	28.0	42.5	1.0	27.0	39.5
	8	0.9	26.0	39.0	0.7	26.0	35.5
	9	0.5	24.0	33.5	0.4	20.5	30.5
5	0				1.4	26.2	38.2[c]
	3	1.8	28.2	43.1			
	6	1.5	26.3	39.3			
6	0				1.4	25.7	37.5[c]
	6	2.1	25.9	39.4			
7	0	2.2	27.6	43.5	1.4	25.3	37.0[c]
	9	1.1	24.2	31.4			

[a] Ratings according to the system proposed by P. F. George.[3] Zero rating is complete solution; 10, no solution.

[b] 1000 lb. per sq. inch. [c] See ref. 5.

Table 5 presents data illustrating the effects of grain size and compound rating[3] on separately cast test bars.

The compound rating is a measure of the completeness of solution, by means of an arbitrary method of designating the amount of beta phase present. As cast, C alloy has a compound rating of 10; completely solution-heat-treated, of zero. As the compound rating is increased to 9 the relative improvement in tensile strength due to quenching is cut in half, but as the grain size increases from 0.004 to 0.007 in. the relative improvement is not affected.

Some special test bars were made in a manner to produce porosity in the reduced section. These were heat-treated, water-quenched and aged, then radiographed, and the porosity was rated according to a previously reported method.[4] Although results were quite erratic, the strength of the quenched bar was always higher than that of an air-cooled bar with a similar amount of porosity. With considerable porosity present, a $1/v$ rating of 250,* the tensile strength of the quenched and aged C alloy was 10 per cent better than that of the air-cooled and aged bar.

Tensile Data on Bars Cut from Castings of C Alloy

To check the laboratory results, several commercial castings were quenched from production furnaces into water at 180°F. The castings entered the water at about 750°F. and were held quietly until they cooled to the water temperature. The castings were then aged, test specimens were cut from them and the tensile values were determined. Table 6 presents the data, including for comparison data from the same type of castings air-cooled and aged. The general improvement in all properties is evident. The grain size of the castings varied from 0.004 to 0.006 in., and there was some porosity present. This accounts for the slightly lower results obtained on the castings as compared with separately cast test bars.

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* This system of rating is based on viewing a radiograph with a variable intensity, calibrated light. Effectively, the contrast between light and dark areas on the radiograph is measured. As the value of $(1/v)$ increases, porosity becomes greater. A rating of 200 means the porosity is just visible on the radiograph while 280 represents about the most porosity normally encountered in commercial practice.

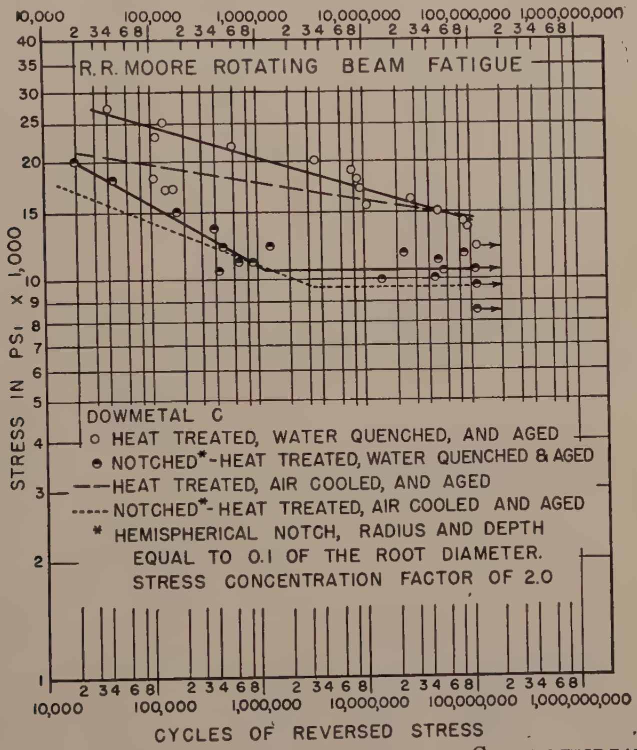

FIG. 7.—FATIGUE STRENGTH OF SEPARATELY CAST C-ALLOY TEST BARS.

FATIGUE PROPERTIES

The fatigue strength of separately cast C-alloy test bars after air cooling and aging and after hot-water quenching from 730°F. and aging was determined. The data are given in Fig. 7, where the experimental points are for the quenched bars; no experimental points are given for the air-cooled curve, to prevent confusion on the graph. The lines shown are through points with a scatter of about ±1500 lb. per sq. in. The line for the quenched and aged plain specimens is drawn through the upper row of points, ignoring the three lower points in the region of 100,000 cycles. Metallographic examination failed to reveal a reason for the position of these three bars, but they are so removed from the rest that the average line does not consider them.

There is improvement due to quenching, which is apparent in both the plain and notched bars; hence the notch sensitivity is the same in both cases. Most of the improvement is concentrated in the low-cycle high-stress portion of the curve.

The fatigue strength of porous C alloy after quenching and aging was compared with air cooling and aging. In this case, if any porosity visible in a radiograph of the specimen were present, no improvement due to quenching was detectable. Thus improvement in the fatigue strength can be effected by quenching only when the material is sound, and even then the improvement is small. All these tests were conducted on the R. R. Moore machine.

TABLE 6.—*Properties of Test Bars Machined from Commercial Castings of C Alloy*[a]

Casting No.	Heat-treatment + Quench + Age				Heat-treatment + Air Cool + Age			
	No. of Samples	% E	Y.S.[b]	T.S.[b]	No. of Samples	% E	Y.S.[b]	T.S.[b]
1	93	1.9	25.5	39.1	17	2.1	22.6	36.0
2	5	3.5	25.2	41.2	7	3.7	21.1	37.7
3	103	3.4	26.7	43.8	20	2.6	25.0	39.9
4	12	4.2	27.1	49.0	22	1.6	22.6	36.3

[a] These castings were all for aircraft-engine application and consequently are thinner in cross section than the separately cast test bars. Bars cut from these castings had machined surfaces. Both of these facts lead to somewhat higher properties than similarly quenched test bars.

[b] 1000 lb. per sq. inch.

There is some question about the sensitivity of this type of test to differences in material. Further work is in progress on tension-tension type of fatigue testing and final conclusions regarding the full benefits to be derived from quenching must await these results.

SUMMARY

The rate of cooling of commercial magnesium-base casting alloys from the solution-heat-treated state is important, as it affects the properties obtained upon subsequent precipitation. Improvement in mechanical properties is effected in all the alloys by increasing the rate of cooling. The improvement obtained is greatest for C alloy, least for R alloy. The improvement is accompanied by microstructural changes that are reasonable with respect to the property changes. The tensile properties of metal in complicated production castings are improved by quenching the castings before aging, at least 10 per cent and even considerably more under the most favorable conditions.

In general, the rate of cooling produced by hot-water quenching of C alloy is beneficial to the properties not only of separately cast sound test bars but also of the casting sections themselves. The most noteworthy improvement is in the combination of high yield strength with good ductility. This is especially evident with low-temperature short-time aging following the solution heat-treatment and quenching.

It is also important that all improvements are gained without introducing significant locked-up stresses in the casting. Thus full design benefit can be taken from the increased property values. Since the endurance limit is not greatly raised by quenching and aging, this process is of practical importance where high strength is important and where better fatigue properties at low cycles are necessary.

Extensive application of the quenching process to commercial castings of magnesium alloys must await tests on the serviceability of castings so treated. A few tests of this nature have been initiated and it is hoped that more will be made so that a true evaluation of the advantages of quenching can be made for commercial castings.

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DISCUSSION

A. E. Flanigan.*—I should like to call the attention of the authors of this paper to the remarkably similar findings issued in September 1943 in the form of a restricted report of the Office of Scientific Research and Development. The latter publication was made available to all agencies concerned with the heat-treatment of magnesium-alloy castings and was given wide circulation. It is based on investigations conducted in 1942 and 1943 at the University of California by Flanigan, Dorn, Cornet and Hultgren.

While the O.S.R.D. report also deals with certain additional subjects not treated in the paper under discussion, it also includes precisely the findings reported by Busk and Anderson. Among others, the following points are treated in detail in the earlier work:

1. The feasibility and desirability of water-quenching magnesium-alloy castings following solution heat-treatment.

2. The prevention of cracking by quenching from temperatures below the range of hot-shortness.

3. The considerable improvement in tensile properties of subsequently aged material, effected through substitution of this treatment for the air cooling generally practiced after solution heat-treatment.

4. The correlation between changes in microstructure and tensile properties effected by the use of the new treatment.

The work of Busk and Anderson appears to confirm the earlier findings in all respects. It indicates, in addition, that the results apply not only to alloys of the Dowmetal C type (which was the subject of the former investigation) but also to other popular compositions. Since the O.S.R.D. report remains on the restricted list, no further comparison will be made at this time.

In closing, the following questions might be asked:

1. Was the previous work not known to Busk and Anderson?

2. Did the authors consult the O.S.R.D. before submitting their paper for publication?

3. Does it not seem that there is a certain inconsistency in that the original work is still regarded as restricted whereas its unacknowledged counterpart is made generally available?

R. S. Busk and R. E. Anderson (authors' reply).—The authors are well aware of the excellent work on the subject of quenching of magnesium casting alloys reported by Flanigan, Dorn, Cornet, and Hultgren. Reference to this was not made in the original paper because of the restrictions placed on the O.S.R.D. report. The authors, of course, have no knowledge of the reason for restricting that report, although it should be mentioned that the O.S.R.D. report covers several subjects other than heat-treatment.

As pointed out by Mr. Flanigan, the present paper coincides in many points with his reported findings. However, the work on which this paper is based was started early in 1941, which is the year before the O.S.R.D. project was assigned.

While good agreement is apparent in the two publications where coincidence of work occurs, the present publication is considerably broader in scope than the O.S.R.D. report. The measurement of cooling rate, determination of the brittle temperature, the role of residual stress, the effect of alloy composition, the interrelation of porosity and quenching, the data from commercial castings, and the effect of quenching on fatigue properties are all subjects covered in the present publication but not in the O.S.R.D. report.

L. W. Eastwood.*—It is especially gratifying at times to have quantitative data on previously known conceptions formulated in a qualitative way only. The data on the temperature at which hot brittleness appears is particularly interesting. The high-zinc alloys, Dow C and H, become brittle at 670°F., while the lower zinc alloy, Dow R, becomes brittle at 700°F. This should also be a measure of their relative hot-shortness in the foundry.

Fig. 2 shows that precipitation begins if the alloys are cooled below 730°F. This means that on a practical basis in the foundry the castings would have to be quenched substantially above 730°F. to be certain that portions of the load had not cooled below this critical temperature. It would seem to me, therefore, since the practical quenching temperature is far above the hot-brittleness range, it would be hazardous to water-quench commercial run of castings. This is particularly true in view of their considerable variations in section thicknesses, complications in designs, etc., which might cause some cracks in certain hot and highly stressed parts of these quenched castings. Quench cracks do not occur consistently, and serviceability tests might miss the damaged parts unless the tests were quite extensive over a considerable period of heat-treating operations. It does not seem, therefore, that quenching commercial castings of the high-zinc alloys would be advisable. Fortunately, the lower zinc alloy does not require water quenching to attain its maximum potential properties. In addition, its hot-brittle range is at a somewhat higher temperature.

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The problem of burning was not covered by the authors in their paper, but this is an important item because burning temperatures of Dow C and Dow H are very much lower than the maximum heat-treating temperatures. Probably this is closely associated with their lower hot-brittleness temperature. On the other hand, the low-zinc alloys have a minimum burning temperature above the normal maximum heat-treating temperature. This is a matter of considerable importance because it is practically impossible to avoid some burning of the high-zinc alloys even under laboratory heat-treatment. While this burning may not appear very important in light sections, such as test bars, it can become quite important in miscellaneous castings where a certain amount of segregation during solidification may occur.

The time required for solution is largely dependent upon the total alloy content and not upon its zinc content, except as it effects the maximum permissible heat-treating temperature. Dow C is not generally regarded as being easy to heat-treat successfully. On the other hand, Dow H is regarded by many as being the most readily heat-treated of the magnesium alloys. In view of the information that is available, it appears that the low-zinc alloys are the most readily heat-treated in a reliable and consistent manner. Perhaps the reputation of Dow H as being an easily heat-treated alloy is due mainly to its lesser tendency to sag and warp during heat-treatment. This is attributed to the lower heat-treating temperature than that used for Dow C or the low-zinc alloys.

R. S. Busk and R. E. Anderson.—Mr. Eastwood has covered a number of subjects, some of which were not discussed in the original paper. We will discuss each item in order.

If by hot-shortness is meant the temperature above which an alloy is brittle, then certainly the brittle temperature is a measure of the relative hot-shortness wherever it is found, including the foundry. If by hot-shortness is meant the relative tendency to crack during casting and solidifying, then the brittle temperature has no necessary relation. As Mr. Eastwood knows, it is very difficult to make magnesium casting alloys crack. But under sufficiently severe conditions, relative cracking tendency is more a function of the total shrinkage than of any other one factor. Thus R alloy has a slightly greater cracking tendency than C alloy.

We believe that the notched panel as used by us represents a very severe test for producing quench cracks. Since half the panel was not under water, that section cooled more slowly than a very thick section immersed in water. The presence of the sharp notch induced large stresses. In addition, a large number of the most complicated aircraft castings have been successfully quenched. If the conditions outlined in Fig. 2 are adhered to, there is very little danger of cracking.

The comment that the lower zinc alloy does not require water quenching to attain its maximum properties is somewhat misleading, since the properties of both the high-zinc and low-zinc alloys are similar when the metal is air cooled. Water quenching does not benefit the low-zinc alloy as much as C or H alloy.

Burning—production of internal voids during heat-treatment—will not occur in any Mg-Al-Zn-Mn alloy unless partial melting occurs. This is easily avoidable in practice with any of the alloys, as examination of production records will disclose.

The time required for solution *at a given temperature* is very sensitive to zinc content. The higher the zinc, the shorter the time. Thus H alloy may be homogenized in 12 hr. at 730°F. while R alloy (the same total alloy content) still requires the same period at a temperature 50° to 70°F. higher. The time required at 730°F. for R alloy would be thousands of hours. The advantage of a lower temperature is real, since sagging problems are minimized.

Factors Affecting Abnormal Grain Growth in Magnesium-alloy Castings

By A. T. Peters,* R. S. Busk,* and H. E. Elliott*

(Cleveland Meeting, October 1944)

One of the problems of the fabricator of metals and alloys is the propensity of some composition ranges toward abnormal grain growth during certain stages of fabrication. In this respect magnesium alloys are no exception among alloys. Fortunately, convenient foundry control methods have been developed by which the abnormal grain growth possible in certain magnesium-alloy castings can be suppressed.

An unusual characteristic of magnesium alloys, however, is that castings of some composition ranges are subject to local grain growth during heat-treatment without the necessity of intentional mechanical stressing of the part prior to heat-treatment. This effect occurs only under certain critical casting conditions, and only in certain alloys of greater than about 8.5 per cent aluminum content, such as C alloy (Mg, 9 per cent Al, 2 per cent Zn, 0.2 per cent Mn) and G alloy (Mg, 10 per cent Al, 0.2 per cent Mn). The first observation of this phenomenon in cast magnesium alloys occasioned much surprise, since it is not observed in other metals. Jeffries and Archer[1] have stated that "the grain size of cast metals, provided they have not been plastically deformed, cannot be changed by heating below the melting point."

The study of the conditions leading to abnormal grain growth in cast magnesium alloys, and of the mechanism of this phenomenon, has led to some very interesting observations. Perhaps the most significant of these was the observation that stresses originating from cooling contraction in magnesium-alloy castings are the only stresses necessary, under certain conditions, to cause local recrystallization and subsequent grain growth in the casting during heat-treatment.

Before recent developments, this phenomenon of abnormal local grain growth was a definite problem in the production foundry on C alloy sand castings. Illustrated (Fig. 1) is a picture of a casting scrapped because of this defect. A mottled effect is produced in coarse-grained areas by suitable etching solutions. The properties of metal in the affected area are much impaired by such grain coarsening. Ultimate tensile strengths of half the normal value have been measured in metal of this nature.

In this paper are described the techniques that have been developed by The Dow Chemical Co. for studying, and in large measure solving, this production problem. Also discussed are studies of the mechanism by which excessive grain coarsening occurs, and the fundamental conditions that produce this effect.

The abnormal grain growth discussed in this paper will be referred to as "germination," since this term has been defined[1] as any process leading to an abnormally coarse grain size. This paper deals only with abnormal local grain growth that may occur during the solution heat-treatment of certain magnesium-alloy castings, as dis-

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[1] References are at the end of the paper.

tinct from any difference in grain size that may exist in the as-cast state.

THEORIES OF ABNORMAL GRAIN GROWTH APPEARING IN THE LITERATURE

Early theory as to the causes of abnormal grain growth attributed this phenomenon to the existence of a critical amount of cold-work in the material prior to annealing, or to a critical temperature of annealing for a given amount of cold-work. Sauveur[2] observed germination in three types of experiments. In the first, a Brinell impression was made in a block of 0.05 per cent carbon steel. Upon heating at 650°C. for 7 hr., a concentric shell of coarse grains was apparent around the impression. Immediately under the Brinell impression, where stress was most severe, grain size was relatively small; neither did large grains appear at a considerable distance from the Brinell impression, where stress was slight. The coarse grain occurred at a distance from the Brinell impression where a critical amount of cold-work was imparted.

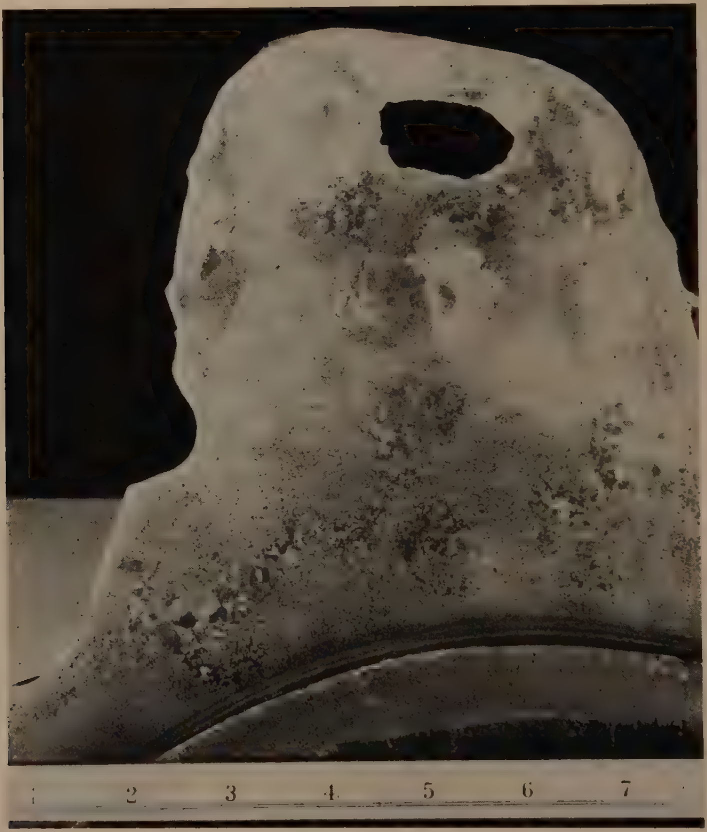

FIG. 1.—A GERMINATED PRODUCTION CASTING.
The mottled appearance is characteristic of the etching effects produced in coarse-grained material.

A bent bar of this material showed the same effect. The unstrained neutral axis of the bar was fine grained after annealing, as were the highly strained external surfaces of the bar, but part way between the neutral axis and the two surfaces, where cold-working was critical, germination occurred.

A third test with this same steel showed that coarse grain occurred upon annealing following the application of 40,000 lb. per sq. in. tensile stress, while if the bar were stressed 38,000 or 42,000 lb. per sq. in. fine-grained structures resulted.

Sauveur observed that these phenomena occurred only in steels having between 0.04 and 0.12 per cent carbon content.

The commonly accepted explanation for these effects has been attributed to Felix Robin.[2] Robin explained the effect of critical stress on the basis of nucleation rates for recrystallization. According to this theory, recrystallization does not occur in understressed material, while in overstressed material, nucleation for recrystallization occurs at so many points that a fine recrystallized grain size results. At a critical stress level, only a few centers of recrystallization occur; all of the cold-worked material recrystallizes on the few stress-free nuclei that form, a coarse grain size resulting.

In studies with silicon-steel sheet, Ruder[3] observed similar effects. His studies showed both that a critical strain produces coarse grain at a given annealing temperature and that a critical temperature of anneal favors grain growth in a material that has undergone a given amount of work-hardening. Rapid heating through the germination (critical) temperature results in a finer grain size than a slow heating rate.

Chappell[4] noticed this same effect in Swedish wrought iron. When tapered bars were stressed in tension, the entire range of stress levels between yield and ultimate was obtained. Annealing of these bars showed coarse grain growth in areas where a critical amount of cold-work had occurred.

Sauveur reproduced excessive grain growth in tapered bars of mild steel, and Carpenter and Elam[5] with alpha brass.

Jeffries[6] observed exaggerated grain growth in tungsten produced by briquetting from tungsten powder containing 0.75 per cent ThO_2. He found that a temperature gradient at a critical temperature level was necessary for germination in this material. Other tests showed that a critical amount of grain-boundary obstruction material (ThO_2) in tungsten

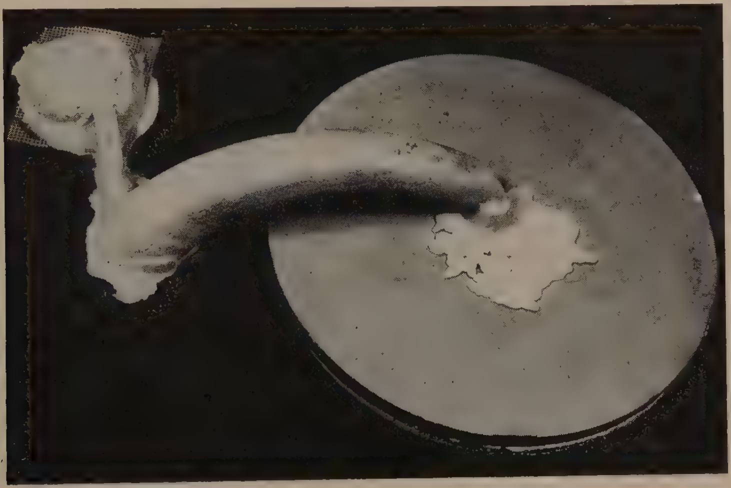

FIG. 2.—CASTING METHOD FOR THE DISK PANEL.

This view shows the heavy disk chill and the horn gate through which the metal enters the mold.

briquettes gave germination at an annealing temperature of 3200°C., and that the heating rate of tungsten containing ThO_2 affects the resultant grain size.

Jeffries and Archer[7] generalized that germination occurs when a grain-size contrast is set up in a generally fine-grained material under conditions that permit absorption of the small grains by the large ones, but not growth among the smaller grains. They reported that such conditions could be set up by strain gradients, temperature gradients, concentration gradients, and obstruction gradients.

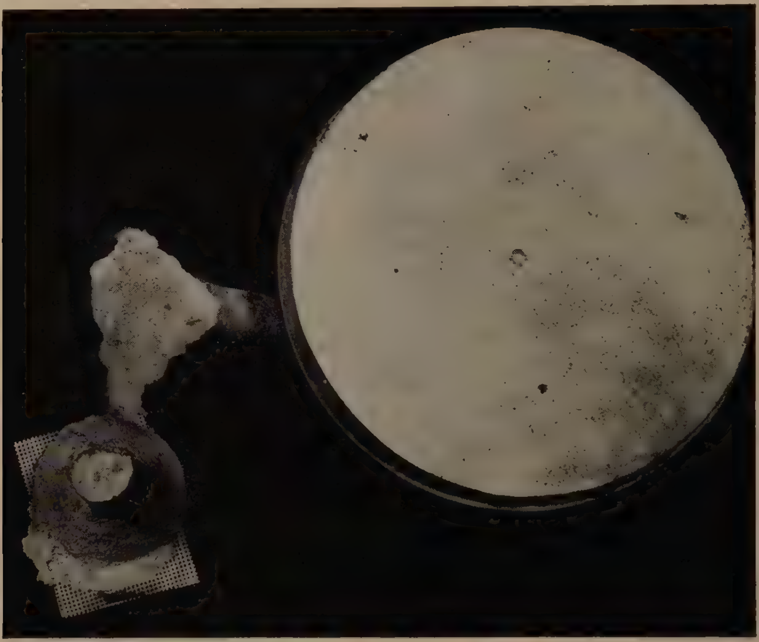

FIG. 3.—CASTING SYSTEM FOR DISK PANEL.
This view shows sprue and runner system, and a top view of the panel in normal casting position.

Eastwood, Bousu, and Eddy,[8] after careful studies of recrystallization in alpha brass, rejected the critical stress theory of germination. Their studies showed that, in alpha brass, just-recrystallized grain size is independent of time or temperature, and dependent only on degree of cold-work. They were unable to produce germination in this alloy by establishing stress or temperature gradients during annealing. Rate of heating to the annealing temperature was found to affect grain size.

Later studies by Eastwood, James, and Bell[9] showed that in high-purity aluminum, as in alpha brass, just-recrystallized grain size is independent of time or temperature.

Cook and Macquarie[10] have reported excessive grain growth in thin sheet copper. After certain forming operations this material was found to develop maximum grain size at a critical annealing temperature, similar to Ruder's observations with silicon steel. This observation appears to be at variance with the laws of normal grain growth advanced by Eastwood, Bousu, and Eddy.

On the basis of present knowledge, it would appear that a critical amount of cold-work or a critical annealing temperature does under certain circumstances cause abnormal grain growth. It is also evident from Jeffries' studies that germination can occur by other mechanisms. The generalization that germination occurs when a grain-size contrast is set up in a fine-grained material appears to be consistent with experimental observations.

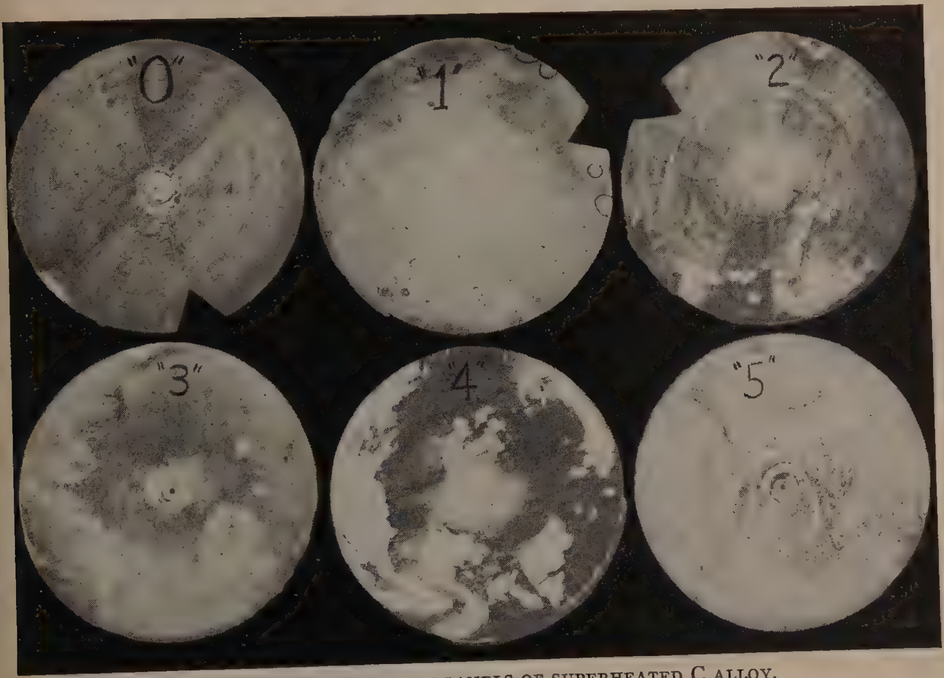

Fig. 4.—Chill-cast disk panels of superheated C alloy.
Sharply defined gray patches are identified as coarse-grained areas. Numerals on panel faces illustrate rating system employed for indicating seriousness of germination.

Experimental Methods

Germination was first observed in experimental chill-cast rectangular panels before the phenomenon was ever seen in production castings. This observation led to attempts to determine the critical conditions of strain and temperatures at which germination would occur. Following methods first used by Chappell,[4] tapered test bars were cast and stressed in tension so that all stress values from the elastic limit to near failure of the piece were imposed. Heat-treatment of this piece caused no grain growth. This experiment was repeated for various alloys, including C alloy, in which the phenomenon was first observed, but germination did not occur.

Later, standard C-alloy test bars were cast in a permanent mold, with the mold coating removed from the reduced section to act as a chill. These bars were stretched in tension various amounts between the yield and failure. No germination occurred. This work was comparable to that by which Sauveur[2] was able to study germination in soft steel. Thus the classical tests that had been found applicable to the study of germination in many other metals failed to produce the phenomenon of germination in cast magnesium alloys.

To study germination, it was necessary to return to the chill-cast rectangular panel in which the effect was first observed. Much difficulty was encountered before it was learned how germination could be intentionally induced in this panel. Finally, it was found that by superheating C alloy (i.e., raising it to 1550° to 1700°F. for 15 min.), casting the panel against a heavy chill, stressing the panel by peening or bending, and giving the panel a thorough heat-treatment, germination could be consistently induced.

In production work, however, germination had been observed without the necessity for peening or otherwise intentionally stressing prior to heat-treatment. Continuation of research work led to the development of a convenient laboratory method by which germination could be intentionally and consistently reproduced without the necessity for intentionally stressing the material. This method duplicated conditions found to produce germination in the production foundry, and so it was adopted for the bulk of research on germination.

The method consisted of casting a disk-shaped panel, 10 in. in diameter and ½ in. thick, on a steel chill of similar thickness. The metal was horn-gated up through a central hole in the chill, as shown in Figs. 2 and 3. The chill had to be left uncoated for germination to occur. Flushing of the mold with SO_2 before pouring prevented surface reaction at the chill surface. A pouring temperature of 1450°F. was sufficiently high to avoid misrunning.

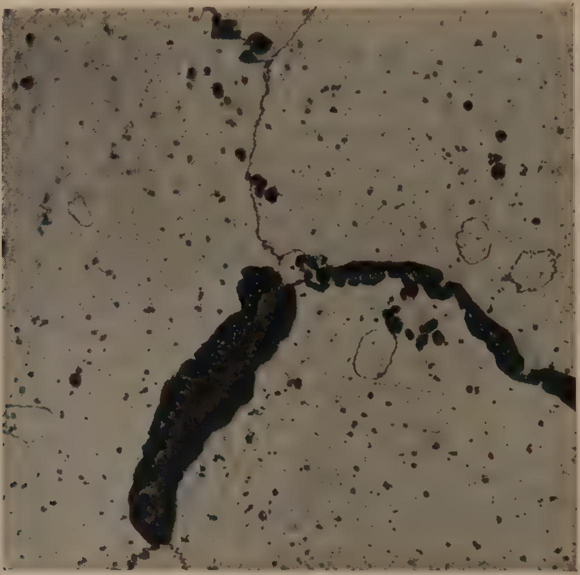

Fig. 5.—Germinated grains in a superheated C-alloy disk panel. Micrograph of panel face. × 70.
Solution heat-treated. Etched with acetic picral.

When panels of superheated C alloy were so cast and then thoroughly solution-heat-treated, exceedingly large grains were formed at the chilled surface of the panel. These grains were often one inch in diameter at the surface, but generally the coarse grains did not extend deeper into the panel than ⅛ to $\frac{3}{16}$ in. The appearance of these panels is shown in Figs. 4, 5, and 6. Of the panels so cast and heat-treated, 80 to 90 per cent germinated.

Certain fundamental prerequisites were at once found to be essential to the occurrence of germination. Both the rectangular panel test and the disk panel test were useful in determining these conditions. In other cases, it was desired to make semiquantitative comparisons of two or more sets of conditions leading to various degrees of seriousness of germination. The disk panel test was adapted to this purpose as follows: A rating system was set up, describing the seriousness of the germination in a disk panel. If no germination occurred in the panel, a zero rating was assigned. If germination completely covered the entire face of the panel, the rating was 5. Intermediate ratings and half-step ratings were assigned to intermediate amounts of area germinated. This rating system is illustrated in Fig. 4. Using it, statistical methods could be used to detect relatively small differences in the germination tendencies of various alloys, heat-treatments, melting treatments, chilling rates, etc

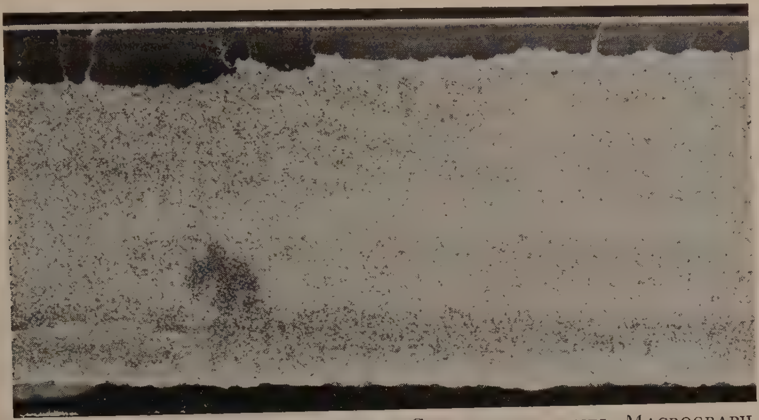

FIG. 6.—GERMINATED GRAINS IN A SUPERHEATED C-ALLOY DISK PANEL. MACROGRAPH OF PANEL CROSS SECTION. × 4.
Solution heat-treated. Etched with acetic picral.

EXPERIMENTAL WORK AND RESULTS

Thermal History of the Metal

First studies of germination by means of the rectangular chilled panel had shown superheating of the metal to be necessary for germination to occur. This observation was confirmed by the disk panel test; in no case was this panel observed to germinate when cast of unsuperheated metal.

Studies in the production-control laboratory showed that germination in production castings could be wholly suppressed by reduction of superheating times and temperatures but, under these conditions, test-bar properties dropped dangerously close to, or below, the minimum of specifications. This method of eliminating germination, therefore, could, not be considered as a control method.

The effect of thermal history of the metal upon germination was further studied by applying various thermal treatments to melts of C alloy, casting disk panels from these melts and using the panel rating to describe the tendency of that thermal treatment to produce germination. The previous thermal history of the melt was found to have a marked effect upon the ease with which germination tendency could be imparted to a melt. A melt of previously superheated ingot required only short superheating times and low superheating temperatures to impart germination tendency, while a melt of ordinary ingot required longer times and higher temperatures. When given a thorough superheating treatment, ordinary ingot and previously superheated ingot both germinated extensively and equally. These observations are consistent with the generally accepted belief that superheating effects are partly retained from one melt to another.

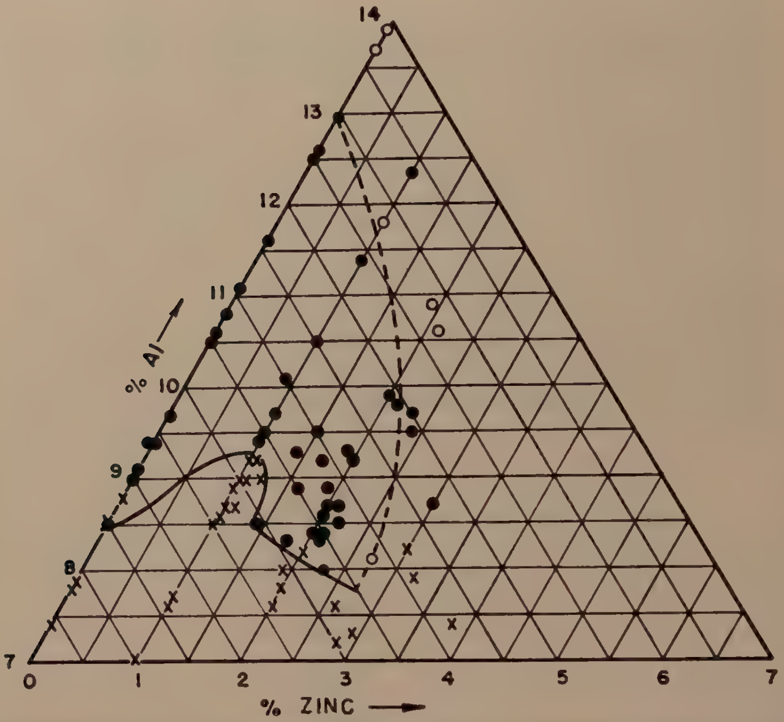

Fig. 7.—Germination in the magnesium-aluminum-zinc ternaries (modified by 0.2–0.3 per cent Mn).

● Alloys germinating in the disk panel.

× Alloys not germinating in the disk panel, when H.T. to zero massive compound.

○ Alloys not germinating in 48 to 100 hours at appropriate S.H.T. temperature.

Solid line: Threshold of alloy content below which germination does not occur in the disk panel.

Broken line: Approximate boundary of alloys germinating in less than 48 hours at appropriate S.H.T. temperature.

Foundry remelt metal could usually be caused to germinate on the panel merely by melting down, raising to the pouring temperature, and pouring. Here the retained effects of repeated previous superheating was sufficient to give germination without the necessity of an additional superheat.

Only one case has been noted in which unsuperheated metal has germinated. In this, a few unsuperheated castings poured in a permanent mold germinated in areas where the casting was heavily stressed during ejection from the mold.

The primary effect of superheating is the reduction of as-cast grain size. Germination has never been found in areas of castings observed to have an as-cast grain size greater than 0.005 inch.

Effect of Alloy Composition upon Germination

1. Mg + Al + Zn.—Early studies of germination by means of the rectangular panel showed that germination did not occur unless the aluminum content of the

alloy was greater than 7.5 per cent. More complete studies were made to find the range of alloys in the Mg-Al-Zn + 0.2 per cent Mn quasiternary system subject to germination in the disk panel. Fig. 7 shows the range of compositions in this system that germinate when cast into disk panels. It is to be remembered that these data describe only the results obtained with the disk panel test; other conditions, such as stressing the panel, might broaden the composition range subject to germination.

The most important feature brought out by this study is that a threshold of aluminum content exists below which germination does not occur, for a given set of conditions. The Zn content affects the value of this threshold slightly, raising it above 9 per cent in the Zn = 1 per cent parameter.

When a C-alloy disk panel is solution-heat-treated, germination does not occur until after about 8 hr. at heat-treating temperature, 4 to 5 hr. after all massive compound has been dissolved.* This would indicate that a high degree of homogeneity, as well as a sufficient aluminum content, is necessary before germination occurs.

Within the range of heat-treating times employed, germination does not occur in the disk panel when the aluminum content is greater than 13 per cent. At this high alloy content, complete solution of the massive compound is impossible. It appears that undissolved $Mg_{17}Al_{12}$ acts as an obstruction agent for the coalescence of adjacent grains.

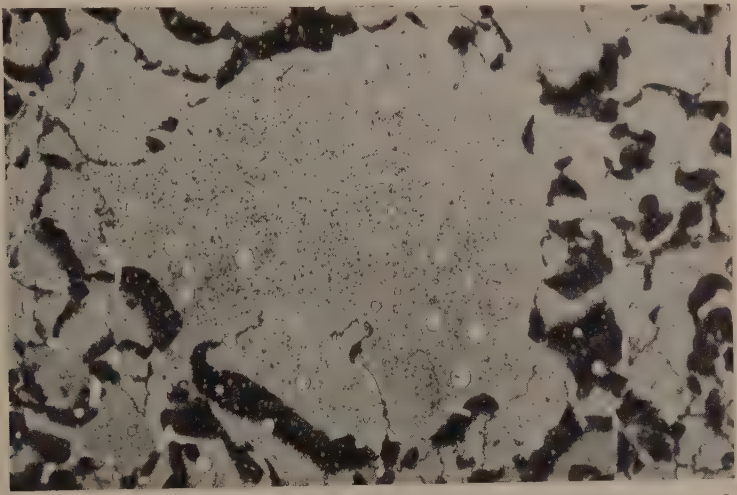

FIG. 8.—GERMINATION IN SAMPLE WITH UNUSUALLY HIGH PRIMARY COMPOUND RATING. × 100.
Mg, 12.6 Al, 0.6 Zn, 0.2 Mn superheated. Heat-treated 48 hours at 808°F. + 48 hours at 770°F. Etched in phospho picral.

Pictured in Fig. 8 is a germinating grain in a disk panel of Mg, 12.6 per cent Al, 0.6 per cent Zn, 0.2 per cent Mn. This sample was given extended heat-treatment at high temperature. There is still a great deal of undissolved compound in and around the germinating grain, but no coring is evident in the photograph and it appears that homogeneity has been approached. The spherical shape of massive compound particles within the germinated grain makes it apparent that the effect of massive compound as an obstruction agent can be overcome by spheroidization during the course of extended heat-treatments.

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* While 16 hr. at 770°F. is the commercial treatment for dissolving massive compound in C-alloy castings, the compound in heavily chilled areas dissolves in only 3 to 4 hr. at this temperature, because of the finely dispersed condition of this phase.

2. *Effect of Manganese on Germination.*—Disk-panel studies showed that a modified C-alloy composition containing no manganese germinates more seriously than normal C alloy. Increasing manganese content to as high as 0.6 per cent did not eliminate germination in the disk panel.

3. *Other Compositions.*—The composition Mg, 10 per cent Al, 0.5 per cent Ag, 0.2 per cent Mn germinated as seriously in the disk panel as C alloy.

The addition of 3.5 per cent Sn to C alloy did not reduce its germinative tendency.

Commercial H alloy (Mg, 6 per cent Al, 3 per cent Zn, 0.2 per cent Mn), as well as C alloy, is used in the production foundry. Commercial H-alloy castings have never been known to germinate in the foundry. Neither have persistent efforts to induce germination in H alloy in the laboratory been successful.

4. *Effect of Minor Additions on Germination Tendency of C Alloy.*—In the course of the search for methods for the control of germination the possibility was investigated that the addition of small amounts of other elements to C alloy might affect its germination tendency, just as the addition of thoria to tungsten retards grain growth in that metal.[6] It was reasoned that a small amount of an added element might act in one of three ways to inhibit grain growth:

a. It might provide grain-boundary obstruction material of the proper distribution to impede grain coalescence.

b. It might produce coring effects, or retard diffusion rates in the solid solution, preventing sufficient chemical homogeneity for grain coalescence to occur.

c. It might raise the recrystallization temperature.

Silicon, strontium, calcium, barium, and cadmium were regarded as the elements most likely, from the appearance of the microstructure, to be effective. Extensive tests were conducted with the disk panel to determine their effect. Silicon was found to be the only one effective in inhibiting grain growth. When 0.15 to 0.30 per cent Si was added as a minor addition to C alloy, germination tendency in the disk panel was much reduced, while the heat-treatability of the alloy was not greatly decreased. Less than 0.15 per cent Si had no effect. However, it is advantageous to keep silicon content as low as possible in casting alloys, so as to avoid the danger of exceeding, by silicon pickup, the 0.3 per cent limit of specifications. The addition of silicon to C alloy was not warranted as a germination-control method, since other control methods not having this disadvantage were found.

Barium, strontium, calcium, and cadmium were not effective in reducing germination, when the panel was given a solution heat-treatment to an acceptably low massive compound rating.

Numerous other elements were given less extensive tests as minor additions to C alloy. None of them were shown to have any beneficial effect.

5. *Effect of Source and Purity of Alloying Ingredients.*—A program investigating the effect of source and purity of alloying ingredients on the germination tendency of C alloy showed no indication that the source and purity of the alloying ingredients had any effect. This study included a comparison of Dow cell magnesium with ferrosilicon magnesium and magnesium obtained from other producers.

Production castings poured from melts of virgin ingot and from melts of remelted scrap plus ingot showed equal amounts of germination.

6. *Comparison of Various Batches of Commercial C Alloy.*—It was suggested that perhaps various batches of commercial C-alloy ingot had inherently different tendencies toward germination. A program was carried out in which 125 different

batches of C alloy were tested by use of the disk panel, to search for such differences. No batch was found that egavconsistently high or consistently low tendency toward grain growth. It was concluded that if such differences existed they were not detectable by available tests.

Effect of Chilling and Stressing on Germination

Both chilling a casting during solidification and mechanically stressing it after solidification increase the likelihood that germination will occur. Germination was found to be possible without the necessity for intentional mechanical stressing but rapid solidification is always found in areas of castings that subsequently germinate. It appears that a very fine as-cast grain size is necessary, regardless of stresses, for germination to occur.

Thus, unsuperheated metal, regardless of stressing, does not germinate either in the peened and chilled rectangular panel, the disk panel, or in production castings. Neither does an unchilled "Chappell-type" tapered test bar germinate, at any stress level between the yield and ultimate produced by pulling in tension.

When very thin panels (⅛ in. thick) are cast in sand without metallic chills, and then stressed very drastically by peening, no germination occurs upon heat-treatment either in peened or in unpeened areas. In production castings a thin section cast in sand will occasionally germinate, but often this can be traced to the presence of a very thin fin of metal formed at a mold or core parting, which would be expected to be very fine grained, owing to rapid solidification of such a thin section of metal. Stressing alone, however severe, has not been observed to cause germination in coarse-grained metal; the as-cast grain size must be very fine.

On the other hand, if as-cast grain size is fine, only very small stresses are necessary for germination to occur. Stresses originating from cooling contraction of the casting are sufficient. Tests have been carried out in which a disk panel was shaken out immediately after pouring, thus allowing the chill to establish a fine as-cast grain size, but not permitting it to produce drastic cooling stresses. Contact thermocouple readings on the chilled surface after shakeout indicated temperatures of 800°F. or above. These panels, cooled in air and then solution-heat-treated, germinated as badly as ordinary panels. Other panels, which were shaken out hot and then transferred immediately to a furnace at 770°F., also germinated upon heat-treatment. This last treatment could have resulted in only small casting stresses, yet with the fine grain produced by chilling these stresses were sufficient for germination. The actual magnitude of the stresses produced by chill-casting a disk panel is not known. Chemical inhomogeneity of the as-cast panel makes X-ray determination of stress magnitude impossible. It is known that any stresses in this panel contributing to germination are not on a "macro" scale, for if the panel is cut into pieces ¼ in. on a side, germination will still occur.

The thermal conductivity and capacity of the chill material appears to have no effect, within rather wide limits, upon germination in the disk panel. Chills ranging in conductivity from stainless steel (cond. = 0.04 c.g.s. units) to copper (cond. = 0.91 c.g.s. units) gave germination very similar in extent to steel (cond. = 0.10). Boiler-plate chills ranging from ⅛ to ½ in. thick gave equal amounts of germination. This does not necessarily mean that the occurrence of germination is independent of the chill material under all casting conditions.

However, if a thin insulating coating is applied to the surface of any of these chills, germination does not occur in the disk panel. While this insulating coating may reduce the initial thermal shock, it does not prevent the chill from performing its normal function of increasing the solidification rate of metal adjacent to it. Chill coating is quite useful as a foundry germination-control measure. The effect of the chill wash evidently is to prevent the formation of exceedingly fine grains at the chill surface.

The possibility was checked that chilling may favor germination by producing a casting texture that might facilitate the coalescence of grains. X-ray studies revealed no texture in the as-cast surface of the disk panel; and, further, no preferred orientation existed among the germinated grains after heat-treatment.

Effect of Heat-treatment on Germination

Earliest work on the germination problem had shown that this defect occurred only if the casting was given a good solution heat-treatment. In the search for control methods for suppressing abnormal local grain growth, a program was conducted to study the tendencies of various heat-treating cycles to produce this effect. This program resulted in the development of a practical control method for greatly suppressing germination in production castings.

It was found that if a casting having germination tendency is given a short exposure to solution-heat-treating temperature, and then given an aging treatment, the casting will have a greatly reduced tendency toward grain growth and may then be heat-treated normally.* The heat-treating cycle appearing to give best results, and now used as the standard C-alloy heat-treatment at the production foundry, is as follows:

2 hr. 500° to 770°F.
6 hr. at 770°F.
2 hr. at 670°F.
10 hr. at 770°F.*

It was observed that the aging stage of the cycle was effective only if it was preceded by a short period at solution temperature. The physical process of aging appeared to exert some effect on the structure of the material, which reduced the tendency to germinate. Another type of heat-treatment that proved successful in suppressing germination involved overheating. If a disk panel was heated for a short period at 850°F., it could then be given a normal solution heat-treatment, with great reduction in germination tendency.*

Experiments were also conducted by which "degermination" was attempted—the breaking down of germinated areas into a fine grained structure. These attempts, which involved stressing and aging treatments, were unsuccessful.

Studies of heat-treating cycles also showed that germination occurs in the disk panel at any temperature sufficient for solution heat-treatment, and that germination is not found in the panel until it has been exposed about 8 hr. to solution-heat-treating temperature.

Production-control Methods Used for Suppressing Germination

Adoption by the production foundry of the 6-2-10 type of solution heat-treatment discussed above was very helpful in suppressing germination to the point where it is no longer a serious production problem.

Other control methods employed are the careful application of chill wash to all chills, and the judicious placing of gates so as to run metal over chills in areas not responding to other control measures.

Metallographic Study of Germination

A very brief metallographic study of the phenomenon of germination was made, in which small areas of disk panels were singled out for metallographic observation during various stages of heat-treatment. In spite of the limited scope of this study, much information was gained as to the nature of the germination phenomenon, and further studies of this kind undoubtedly will yield additional information as to the mechanism by which germination occurs in magnesium alloys.

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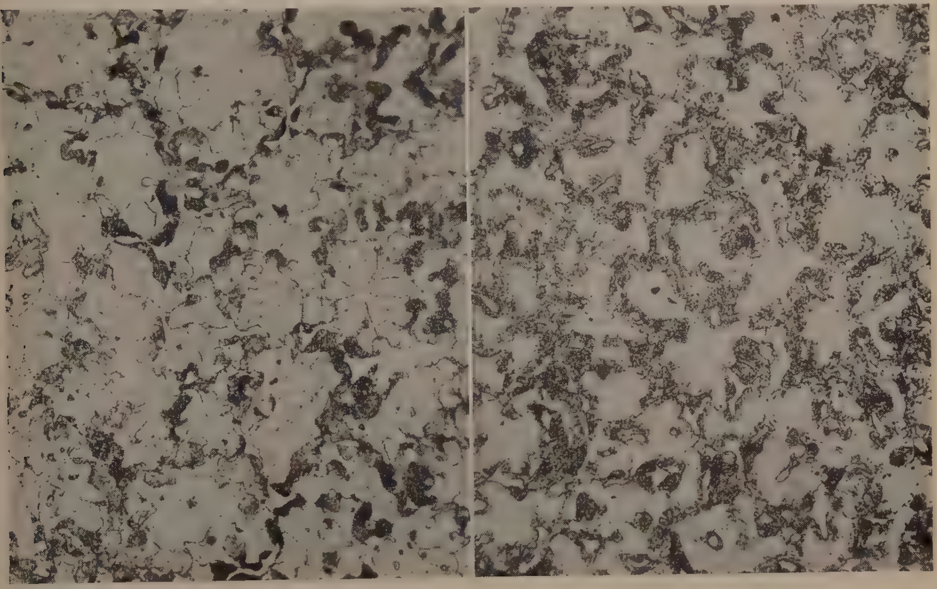
* A patent covering this type of heat-treatment has been applied for.



a *b*

FIG. 9.—SUPERHEATED C-ALLOY DISK PANEL. × 250.

a. Etched in acetic picral, heat-treated for 1 hour at 600°F. and etched in acetic glycol. Shows that no recrystallization occurs at 600°F. Section polished and then heat-treated.

b. Etched in acetic picral, heat-treated for 15 minutes at 700°F. and etched in acetic glycol. Shows recrystallization occurs at 700°F. Section polished and then heat-treated.

Since it was known that only very small stresses are needed in the disk panel for germination to occur, it was questioned whether recrystallization was occurring prior to germination. It was considered possible that in magnesium alloys grain growth may occur by coalescence of only slightly strained as-cast grains, without the necessity for a strain-relieving recrystallization stage, just as unrecrystallized grains have been observed to grow in 70-30 brass.[11] Accordingly, a number of samples were cut from a superheated C-alloy disk panel. These samples were polished very lightly on the chilled face, and accurate as-cast grain sizes were read; the etchant was acetic picral.* Average grain diameters for these samples ranged from 0.0015 to 0.0025 in. These samples were then heat-treated for 15 min. and for 1 hr. at 400°, 500°, 600°, and 700°F. Following heat-treatment, the samples were again etched *very lightly and without an additional polishing operation*. The etchant this time was acetic glycol,* and some of these samples showed two sets of grain boundaries—the original as-cast boundaries and the new recrystallized grain boundaries. Fig. 9*a* shows the sample heat-

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* Acetic picral etchant is prepared by adding, just before use, 10 ml. of glacial acetic acid to 100 ml. of picric acid saturated in 95 per cent ethanol.[13]

* The composition of acetic glycol etchant[14] is as follows:

	Per Cent by Volume		Per Cent by Volume
Ethylene glycol...	60	Conc. nitric acid..	1
Glacial acetic acid.	20	Distilled water...	19

treated one hour at 600°F. Only the as-cast grain boundaries are seen, no recrystallization having occurred. Fig. 9*b* is the sample heat-treated 15 min. at 700°F. Recrystallization has clearly occurred.

and Fig. 11*c*, after one hour at 770°F. (solution-heat-treatment temperature). In Fig. 11*c* the casting dendrites are seen in the center of each grain, showing that no shift in grain boundaries has occurred.

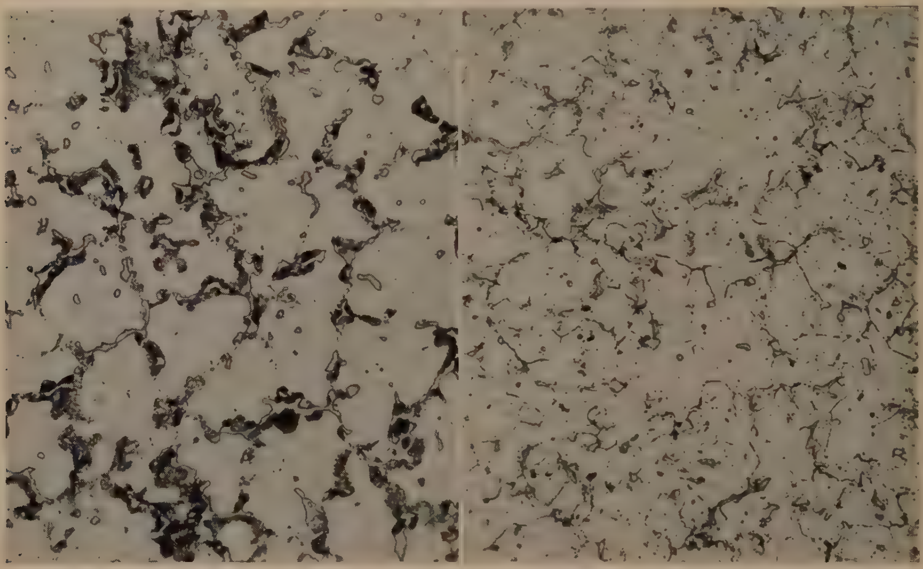

Fig. 10.—Superheated C-alloy disk panel. × 250.

a. As-cast and etched in ethyl glycol, showing as-cast structure.

b. Heat-treated for 15 minutes at 700°F. and etched in acetic glycol, showing recrystallization occurring at 700°F. Section heat-treated before polishing.

To show that this effect was not due to the initial polishing operation, additional samples were heat-treated 15 min. at 700°F. before any polishing. Fig. 10*b* shows the recrystallization produced by this treatment, while Fig. 10*a* shows the as-cast structure of a similar section. Recrystallization occurred to a depth of about ⅛ in. in these sections.

Sections were also cut from panels of unsuperheated C alloy and of superheated H alloy. These were heat-treated for periods of 15 min. at 500°, 600°, 700°F., and solution-heat-treatment temperature, and one hour at solution-heat-treatment temperature. Fig. 11*a* shows the as-cast unsuperheated C-alloy structure: Fig. 11*b* shows the structure after 15 min. at 700°F.; Recrystallization was not detected in unsuperheated C alloy for any thermal treatment.

Fig. 12 shows the superheated H-alloy structure after one hour at 730°F. (solution-heat-treatment temperature). Casting dendrites are clearly seen in the center of each grain, except for occasional scattered grains, through the dendrites of which grain boundaries may be seen to pass.

It is thus clear that recrystallization occurs in the fine-grained surface of a disk panel of superheated C alloy, this type of panel ultimately germinating. When a relatively fine-grained panel of superheated H alloy is cast, or a coarse-grained panel of unsuperheated C alloy, recrystallization does not occur to any comparable extent

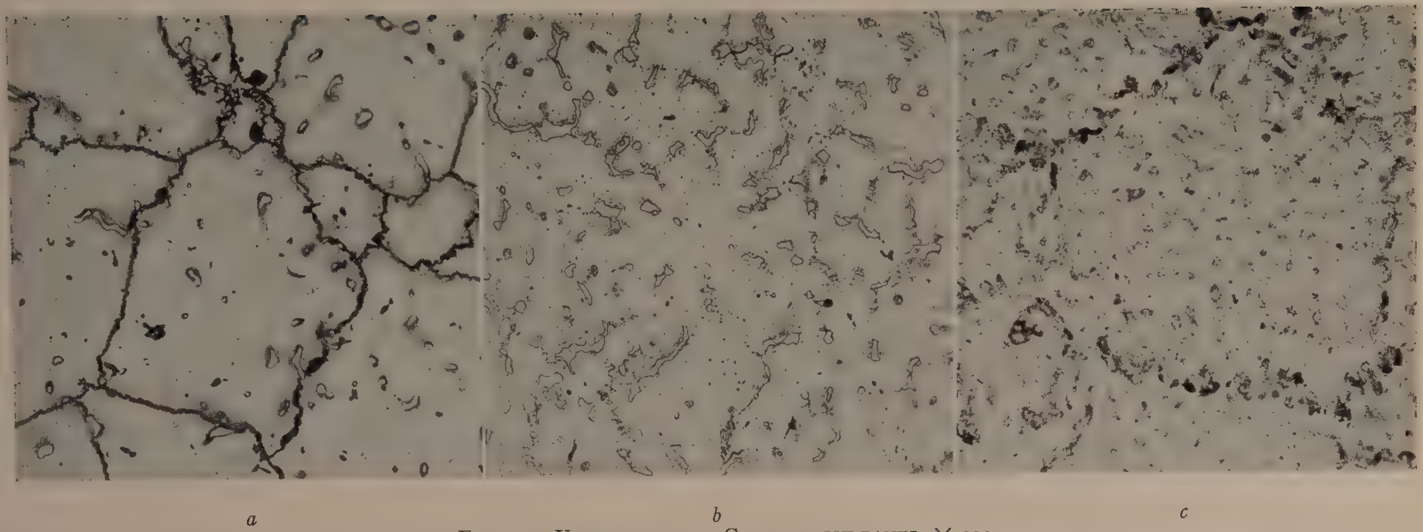

FIG. 11.—UNSUPERHEATED C-ALLOY DISK PANEL. × 200.

a. As-cast and etched in acetic glycol showing as-cast structure.
b. Heat-treated for 15 minutes at 700°F. and etched in acetic glycol showing no recrystallization at 700°F. Section heat-treated before polishing.
c. Heat-treated 1 hour at 770°F. and etched in acetic picral showing no recrystallization at 770°F. Section heat-treated before polishing.

at or below ordinary solution-heat-treatment temperatures; panels of neither type will germinate.

A series of micrographs shown in Figs. 13 to 17 was taken of the same area of a sample from a superheated C-alloy disk panel at various stages of heat-treatment. A sample 1 in. square was sawed from a disk panel, and then carefully ground and polished by mechanical methods. A small square, about 0.05 in. on a side, was then marked on the sample by scratching with a razor blade. This area was photographed at various stages of heat-treatment. Fig. 13 was taken after 2 hr. at 500° to 750°F. plus 5 hr. at 750°F.

After five additional hours at 770°F., germination had started at a saw mark and extended into the lower left-hand corner of the area under observation. Fig. 14 is a micrograph of the specimen at this stage, and shows a substantial increase in general grain size of the specimen over the previous stage. Prior to examination, the specimen was this time stain-etched with acetic picral. This technique has the remarkable effect of producing the grooved appearance of the crystal surface observed in the photograph. There appears to be a series of roughly parallel grooves across the face of each grain, and the direction of these grooves appears to be a characteristic of the grain. The grooves of each grain retain their directional nature during heat-treatment and re-etching, unless the grain is absorbed by another, in which case the directional characteristics of the second grain are assumed.

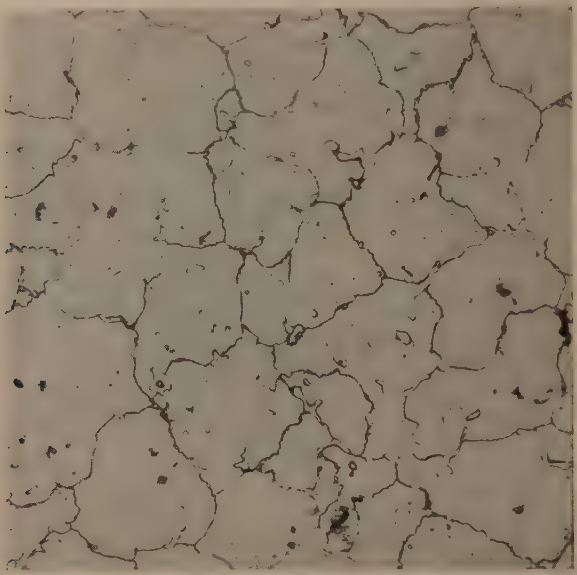

FIG. 12.—SUPERHEATED H-ALLOY DISK PANEL SHOWING VERY LITTLE, IF ANY, RECRYSTALLIZATION AT 730°F. × 250.
Heat-treated for 1 hour at 730°F. Etched in acetic picral. Sample heat-treated before polishing.

Fig. 15 shows the same area after an additional hour at 770°F. The germinant grain has spread rapidly over part of the area, by-passing four grains in the process.

The next photograph (Fig. 16) was taken after an additional 2 hr. at 770°F.; the germinant grain has further spread.

Fig. 17 was taken after 2 hr. more at 770°F. The germinating grain has spread still farther, but rate of growth has slowed considerably since this grain was first observed. Although the same area, as far as possible, is illustrated in Figs. 13 to 17, complete correspondence of grain boundaries is not attained because of the necessary polishing and etching between pictures. The correspondence is considerably better between adjacent pictures in Figs. 14 to 17 than between Figs. 13 and 14.

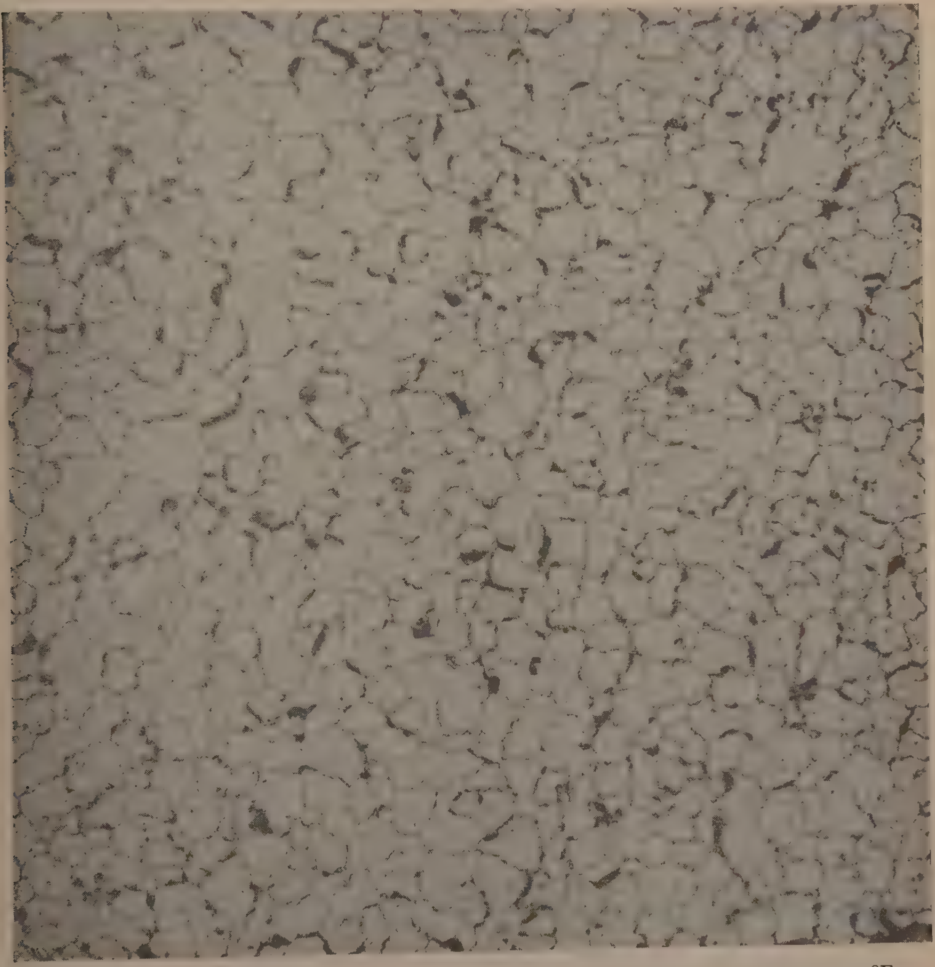

FIG. 13.—C ALLOY HEAT-TREATED 2 HOURS FROM 500° TO 750°F. PLUS 5 HOURS AT 750°F. Original magnification 150; reduced about ¼ in reproduction. Etched with acetic picral.

DISCUSSION OF RESULTS

The most important feature brought out by the metallographic study was the fact that a *general* recrystallization precedes the germination process. This initial recrystallization is complete after a short period at 700°F., while germination is not apparent in the casting until after 8 hr. at 770°F. The pictures clearly show that germination does not occur by the formation of scattered nuclei for recrystallization upon which all of the work-hardened material recrystallizes, as visualized by Robin as an explanation for germination effects in critically stressed metals. Germination in the alloys studied in this paper occurs by a different mechanism.

The first stage of this mechanism is a general recrystallization of the fine-grained, slightly stressed material. The just-recrystallized grain size is very small, less than 0.001 in. After recrystallization, coalescence of the recrystallized grains takes place, and the extremely large grains are formed during this coalescence stage.

Coalescence does not occur uniformly throughout the structure. It starts earlier at some spots in the casting than at others, and thereby sets up grain-size contrast in the material. A condition results that Jeffries and Archer[7] have described as ideal for germination; namely, that a few coarse grains are present in a generally fine-grained material. These coarse grains, formed by early coalescence at a few spots in the casting, begin to grow rapidly at the expense of fine grains surrounding them, when sufficient homogeneity has been attained in the casting to permit coales-

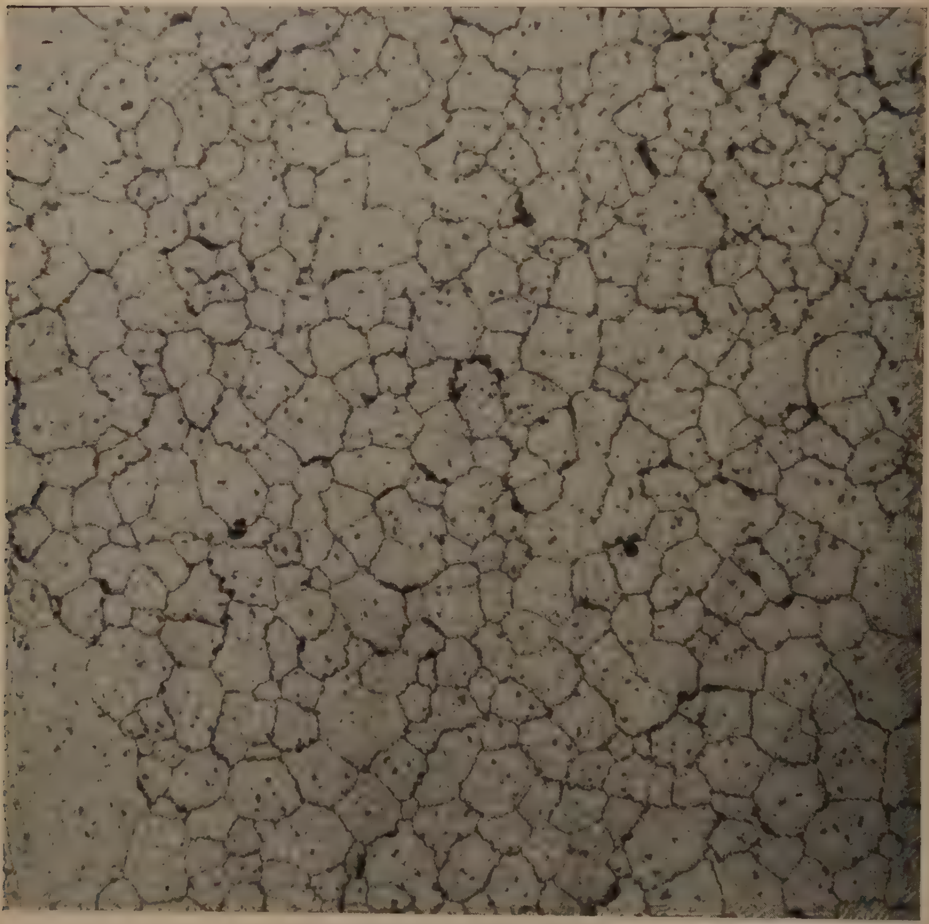

FIG. 14.—C ALLOY.
Same area and magnification as in Fig. 13, taken after an additional five hours at 770°F. followed by light repolishing and etching with acetic picral stain etch. Note entrance of germinant grain in lower left corner, and general grain enlargement throughout area.

cence. This process of rapid growth of coarse grains through fine-grained metal is clearly shown in the micrographs of Figs. 13 to 17. In the samples shown here, grain-size contrast was set up by early coalescence of recrystallized grains at saw cuts. For some reason such drastic stressing appears to decrease the time required for coalescence to begin after recrystallization. (It may be that drastic stressing gives a finer just-recrystallized grain size, which would favor rapid coalescence.)

It has not been definitely shown why coalescence starts earlier in some parts than in other parts of a casting that has not been intentionally stressed. Several plausible theories have been advanced.

First, it may be that owing to flow conditions in filling the panel and consequent cooling conditions, cooling stresses in the

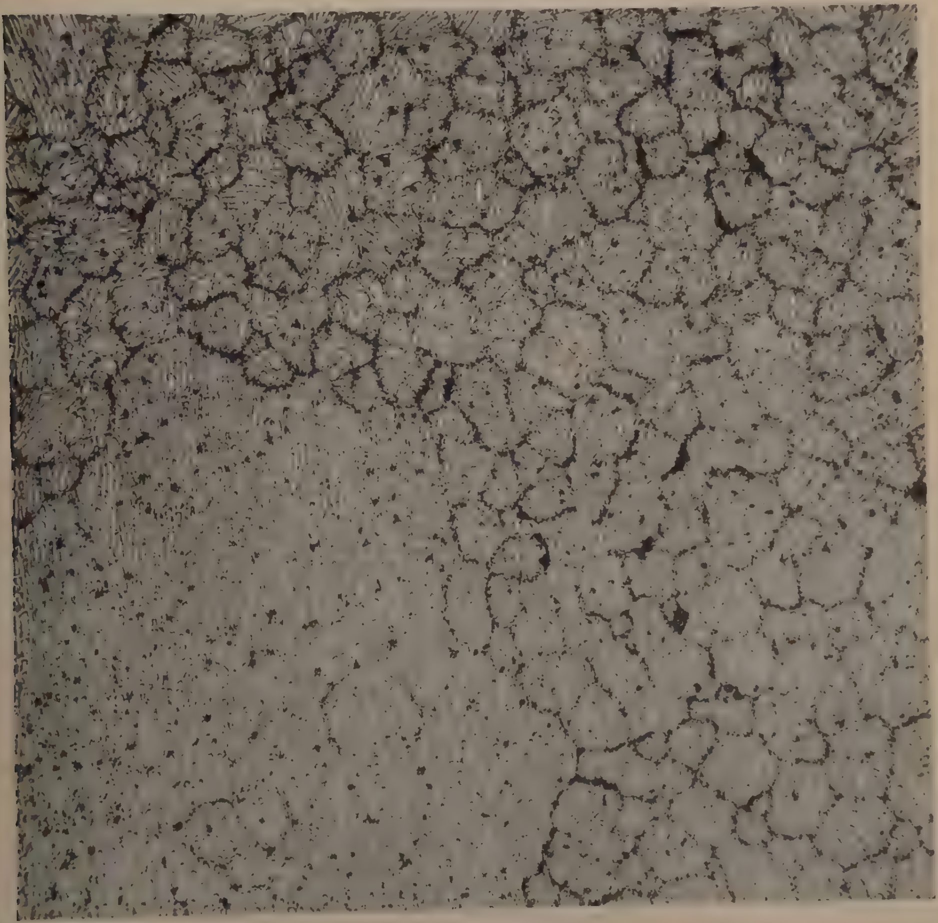

FIG. 15.—C ALLOY.

Same area and magnification as in Fig. 14 after an additional hour at 770°F., followed by another light repolishing and etching with acetic picral stain etch.

The germinant grain first observed in Fig. 14 has rapidly advanced into the central area. Four grains have been enveloped but remain essentially intact. Individual grains can be readily identified in this series of micrographs.

panel vary sufficiently from point to point to promote grain coalescence in one area more strongly than in another. In light of this theory, the effectiveness of the aging and overheating types of heat-treatments could be very simply explained, since both types of heat-treatment are in the direction of increasing atomic mobility and thus of relieving or redistributing stresses.

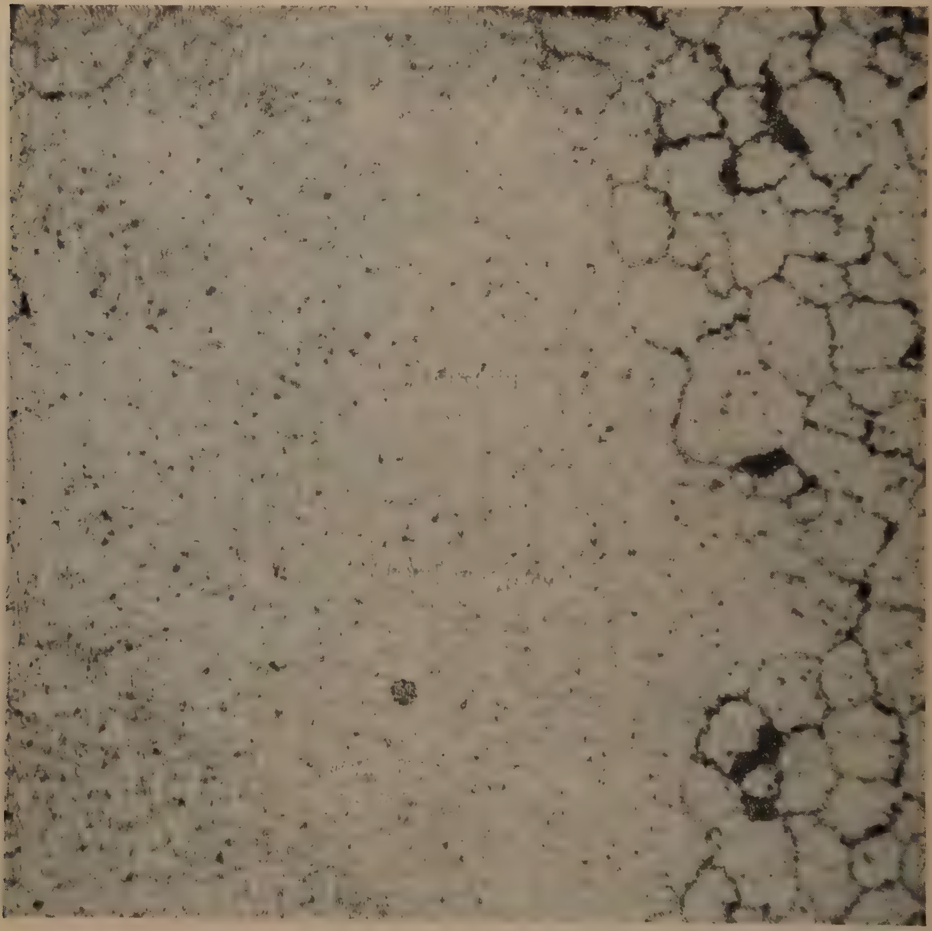

FIG. 16.—C ALLOY.

Same area and magnification as in Fig. 15 after an additional two hours at 770°F. followed by light repolishing and acetic picral stain etch.

The germinant grain has progressed rapidly, and the four enveloped grains have been absorbed.

Second, it is known that the occurrence of germination requires, on the one hand, that a threshold aluminum content be exceeded, and on the other hand, a high degree of local homogeneity. It may be that local segregation at the heavily chilled surface may produce composition conditions that favor earlier coalescence at one spot than at another. Earlier coalescence would be expected to occur at places where:

1. Aluminum content is high.
2. Individual grains are homogeneous.
3. Adjacent grains have the same lattice

constants, which would necessitate equal aluminum and zinc contents.

This theory might explain the effectiveness of the aging type of heat-treatment, since aging, followed by solution heat-treatment, tends to generally homogenize a polycrystalline structure, and such homogenization might prevent earlier coalescence at one point in the casting than in another.

Third, it may be that at scattered spots through the casting areas exist just after recrystallization where a number of grains have similar orientations, which might favor the early coalescence of grains at these points.

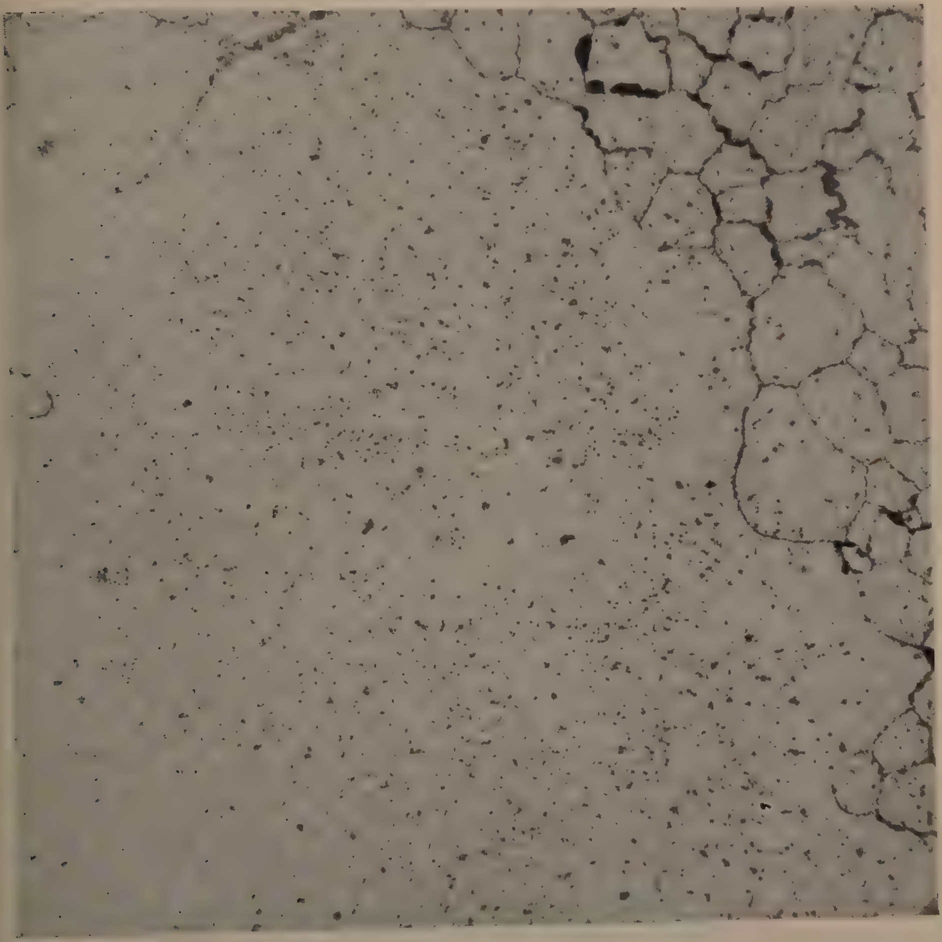

FIG. 17.—C ALLOY.
Same area and magnification as in Fig. 16 after an additional two hours at 770°F. Although growth of the germinant grain is continuing, it is at a greatly reduced rate.

In view of the fact that a general recrystallization occurs before germination takes place, as well as the facts that chill conductivity does not greatly alter the extent of germination and that shaking out while hot does not alter the extent of germination, it is difficult to believe that a critical stress level is required for germination to take place in chilled portions of castings, although stress and possibly stress contrast contribute to the effect. In heavily worked, fine-grained magnesium alloys, as in wrought products, critical amounts of cold-work have been observed to give grain-coarsening effects—in the peened rectangular panel, for example, coarse grain has been observed in concentric shells around peening impressions—but when germination occurs at chilled sections of castings not intentionally stressed, the mechanism of grain growth seems not to be dependent upon a critical amount of stressing.

Germination is seldom complete in the chilled surface of a disk panel; nearly always there are ungerminated areas of considerable extent—probably because uniform grain growth is constantly occurring in regions that are homogeneous enough to coalesce but which have not yet been reached by a germinant grain. When the germinating grain does reach such areas, the grains are large enough to have considerable orienting power themselves, and the energy level of a given grain will not be reduced sufficiently by coalescence to overcome reluctance to change its orientation. Figs. 13 to 17 show the rapid growth of germinant grains through fine-grained material, and the slowing down of growth as coarser grained material is encountered.

The failure of unsuperheated C-alloy disk panels to recrystallize was very surprising. It is well understood that a coarse-grained material worked by the same amount of tensile, torsional, or compressional stress as a fine-grained material, has a higher temperature of recrystallization,[12] but it is remarkable that while the superheated C-alloy disk panel recrystallizes at temperatures below 700°F., the unsuperheated panel, cast under identical condition, fails to recrystallize at 770°F. We can only conjecture as to whether this is purely an as-cast grain-size effect or an effect of the superheating process that is not yet understood.

SUMMARY

Cast magnesium alloys of certain composition ranges and under certain casting conditions display the unusual property of undergoing local grain growth during heat-treatment without the necessity of intentional mechanical stressing. Control methods have been developed for suppressing germination; among these, special heat-treating cycles are particularly effective and are in industrial use, but chill coating and intelligent placing of gates are also helpful as additional control measures.

Germination occurs only in certain composition ranges in magnesium alloy castings, and only when a fine as-cast grain size is obtained by superheating and chilling. Stresses add to the likelihood of germination, but in a fine-grained structure even small microstresses are sufficient.

Metallographic studies show that germination occurs during heat-treatment by a general recrystallization of the as-cast structure, followed by the early coalescence of grains at a few spots throughout the casting and by growth of the germinant grains so formed.

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DISCUSSION

(*M. A. Hunter presiding*)

M. A. Hunter.[*]—In presenting the paper, Mr. Elliott mentioned that there is a limit of aluminum content in which this germination can occur. I have met it in a parallel situation in sheet magnesium of composition of 6.5 aluminum and a little less than 1 per cent of zinc. Under certain rolling conditions, that sheet when heat-treated can grow enormous grains. It is not a case exactly parallel to his, because he is dealing with castings. In a sheet material, we were dealing with a material that originally was superheated, 6.5 per cent aluminum, and that material can germinate to a high degree.

R. T. Wood.[†]—I especially admired the metallographic work, which showed that recrystallization takes place prior to germination. Perhaps I admire that so much because we looked for it and could not find it. Our work on germination parallels and largely confirms the things told here.

However, we have observed a few discrepancies and I might mention them for their general value or information on the subject. First, we have some samples that show germination, which were cast in sand against extremely heavy chills, and it appears that an extremely fine inherent grain size is not always necessary in order to get germination. If the chill is severe enough, apparently an inherent grain size of the order of magnitude of 0.01 in. will germinate.

The authors have concluded that absolutely complete solution of the beta phase is not necessary. It has to be nearly complete, but we also have observed areas of germinated grains with beta constituent out of solution.

The third thing we have observed is rather queer, and we have no very good explanation for it. It is that germination can start as much as ½ in. away from the chilled surface. The chilled surface will remain apparently fine-grained and the sample will have an area of extremely coarse grain perhaps ½ in. from the chilled surface. Just why the germination starts so far from the source of stress, we are unable to explain.

The next thing that is rather puzzling is that the authors were unable to obtain germination on the special tapered test bars, whereas it is a rather common occurrence to find germination starting from a very minute stress, such as that induced by a saw cut. I wonder if the authors have any explanation of why a minute stress from a saw cut will produce germination while none was observed during the experiments with tapered test bars.

There is one other point that I might mention, and it is in line with what Professor Hunter has said; namely, that in magnesium alloys germination is fairly prevalent if the heat-treating temperature is high enough. Very slight stress, such as that obtained when machining a test bar from a piece of extruded rod, for instance, will often induce germination if that bar is subsequently heat-treated. I do not recall the minimum aluminum content of alloys in which this phenomenon has been observed but it has been at least as low as 6 per cent aluminum; and some alloys that require extremely high heat-treating temperatures, for instance one containing 6 per cent silver, 3 per cent zinc and 3 per cent aluminum, are extremely prone to germination. In this alloy germination will occur just from the stresses remaining after hot extrusion. This marked tendency toward germination was one of the reasons why the alloy was not developed commercially.

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[*] Professor of Metallurgical Engineering, Rensselaer Polytechnic Institute, Troy, N. Y.

[†] American Magnesium Corporation, Cleveland, Ohio.

H. E. Elliott.—We have never observed grain growth or the germination where the grain size was greater than about five-thousandths of an inch. I do not know whether that is a matter of just not making the right tests or whether it is a matter of difference in the way we measure our grains, but we have never observed anything like that. Neither have we observed subsurface germination—germination underneath the chilled area of the casting.

A. T. Peters.—I would like to make an addition. In some work that was done prior to that to which Mr. Elliott referred, we did observe some subsurface germination of the type Mr. Wood has mentioned.

H. E. Elliott.—I was thinking of the type of germination that occurs on a chilled surface of a casting that has not been heavily mechanically worked. Yes, sometimes you find a shell of germination around a peening impression, as in the rectangular chilled panels discussed.

A. T. Peters.—Mr. Wood mentioned that he has observed germination without complete solution occurring. We also have observed germination under those conditions. However, we have found under those conditions that a good heat-treatment was required so as to obtain a uniformly high level of solution throughout the grain. We found it on a sample of high aluminum content and we did observe germination under those conditions.

You also asked why we did not obtain any germination in the Chappell type of bar, the tapered bar. We believe that is in order with our observation, that we do not generally get germination unless there is chilling of a drastic nature. Those tapered bars when cast were not chilled.

We also agree that germination on wrought alloys is apparently something a little distantly related to the thing we are concerned with, and we are very prone to get germination, then, in alloys of lower aluminum content, just as Mr. Wood reported.

J. D. Hanawalt.*—Would you give the critical aluminum content as 7.5 per cent Al?

H. E. Elliott.—On the rectangular panels, we found that germination would occur when the aluminum began to exceed 7.5 per cent; with the disk-shaped panels, more heavily chilled and not peened, around 8.4 per cent aluminum and 2 per cent zinc were present.

J. D. Hanawalt.—I think it would be worth pointing out in that connection that one would consider your test panel a very severe test and much more likely to cause germination than any normal condition in the production foundry.

H. E. Elliott.—We feel that very rarely are conditions so favorable to germination set up in normal production foundry practice.

R. T. Wood.—We encountered another curious phenomenon with respect to germination. It was in connection with the casting of permanent-mold test bars. They are cast in a split mold. As the mold becomes worn, a flash tends to run the length of the test bar and germination is quite likely to start in that flash region during the heat-treatment of the test bar.

We found, however, that in a great many instances germination could be prevented by grinding off the flash before heat-treatment. If you remove the stress, you apparently reduce the tendency toward germination.

H. E. Elliott.—Yes, we have had a corresponding experience in sand casting. On some areas of castings that are very thin but do not have metallic chills, we have observed germination, but nearly always in those cases we were able to trace that to the existence of a core or mold parting and a thin flash of metal, which must have been very rapidly solidified and hence given a very fine as-cast grain size. Such a place as that evidently allowed germination to start.

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* Dow Chemical Co., Midland, Michigan.

Grain Refinement of a Carbothermic Magnesium Alloy by Superheating

By Ralph Hultgren,[*] Member, David W. Mitchell,[†] Junior Member and Bernard York,[‡] Member, A.I.M.E.

(New York Meeting, February 1945)

It is a well-known fact that magnesium-alloy castings are apt to be coarse grained if the melt is not superheated several hundred degrees above the melting point before casting. (The casting temperature varies according to the shape of the mold. A typical casting temperature is perhaps 1400°F.) British practice is to heat to 900°C. (1650°F.) for 15 min., cool rapidly to casting temperature, and cast.[1] In Germany superheating is carried out at 850° to 900°C. (1560° to 1650°F.) depending on the amount of scrap used. It is stated that further refinement will be obtained by prolonging the period of superheating or by increasing the superheat temperature to 950°C. (1740°F.).[2] In the United States superheating is carried out at 1600° to 1700°F. (871° to 927°C.), perhaps even higher in some places. It is stated that superheating effects are found as low as 1500°F. (816°C.), but several hours are required.[3]

These commercial treatments lead to grain sizes in sand castings that may vary from 4 to 8 grains per sq. mm.[§] in heavy sections and from 60 to 100 in ½-in. sections to perhaps 380 in thin sections. It is also generally known that the refining effect of superheating is lost if the melt is held for some time at lower temperatures before casting.

Aside from these very qualitative statements, there is little to be found in the literature as to the effect of temperature and time of superheat on the final grain size. Because of the uncertainty of these factors, the Office of Production Research and Development of the War Production Board placed a research contract with the University of California, supervised by the War Metallurgy Committee. This research, which was done under the "Restricted" Project NRC-550, is the basis of this paper, which has been released for publication by the O.P.R.D.

The material studied was an alloy prepared from carbothermic magnesium. The temperatures required for grain refinement proved to be widely different from those used in practice, as described in the statements in the first paragraph. This difference is attributed to the fact that the magnesium in the specimens was of carbothermic origin instead of the electrolytic magnesium in common use.

MATERIALS AND METHODS

The magnesium alloy studied was one of the most popular sand-casting alloys, with a nominal composition of 9 per cent aluminum, 2 per cent zinc, and 0.1 per cent (minimum) manganese and the balance magnesium. This is designated

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[1] References are at the end of the paper.

[§] The frequently used designation, average grain diameter, equals

$$\frac{1}{\sqrt{\text{no. of grains per unit area}}}.$$

as alloy No. 17 by the American Society for Testing Materials and hereafter will be referred to as No. 17 alloy. The metal was supplied by the Permanente Metals Corporation. It was prepared from magnesium produced by the carbothermic process[4] at Permanente, Calif. The composition of the heat used was given by the Permanente Corporation as: Al, 8.62 per cent; Zn, 2.07; Mn, 0.49; Si, 0.2 (max.); Cu, 0.04 (max.); Ni, 0.005 (max.); other impurities, 0.2 (max.); Mg, balance.

In melting, fluxing, superheating and casting so many deviations are possible in practice that a given heat cannot be duplicated. Since accidental deviations may have a significant effect on grain size, it was decided, wherever possible, not to compare different heats with each other, but to split the single heats into portions, each portion being given a different treatment.

For the majority of the experiments the following procedure was used: A 5-lb. section of a 20-lb. ingot of magnesium alloy was melted in a Tercod crucible in a gas-fired furnace, and fluxed thoroughly with about ⅔ lb. of Permanente No. 7* refining flux at 1300° to 1350°F. (704° to 732°C.).[3] It was then cooled to about 1250°F. (677°C.) and a portion weighing approximately one pound was ladled into an iron crucible contained in an electric furnace at about 1250° to 1300°F. (677° to 704°C.) and was covered with Permanente No. 21† covering flux. The furnace and contents were then heated to about 10°F. below the desired superheat temperature and the crucible was removed, placed in a holding furnace and held for a measured period of time at superheat temperature. The time of heating, determined from an iron-cased pyod in the metal, was about one minute for each 20° to 30°F. Maximum fluctuation in temperature in the holding furnace was ±10°F.; usually the fluctuation amounted to no more than a few degrees.

After superheating, the crucible was transferred to a third electric furnace, which was at the superheat temperature. The current was turned off and furnace and contents were cooled to slightly above casting temperature. The rate of cooling was about 10°F. per min. The crucible was then placed in a holding furnace at casting temperature and allowed to equalize its temperature for about two minutes.

At the end of the equalizing period, the crucible was removed and the metal was cast into a heated cast-iron mold, cold baked sand mold, and a heated baked sand mold. The heated molds were at about 360°F. (182°C.). Baked sand molds were used instead of green-sand molds in order to eliminate such variables as moisture content, porosity and effect of inhibitors. Four crucibles of metal were treated in this fashion from each melt, varying the superheating conditions as desired.

The iron crucible in which superheating was usually done is shown in Fig. 1. The vertical part was cut from a pipe guaranteed to be low in nickel and the bottom was a welding cap welded to the pipe. The heating and cooling were done in cylindrical electric resistance furnaces with the heated zone 5 in. in diameter and the opening in the top. The bottom of the furnace also contained a heating element. The holding furnaces were designed for precise temperature control and were remarkably accurate when care was taken that the crucibles introduced were already near the temperature of the furnace. Spectrochemical analysis showed no significant pickup of impurities in this process. One of the holding furnaces is shown in Fig. 2.

The castings were all of the same shape (Fig. 3), designed for low turbulence in casting. The section examined was the cross section of a 1-in. cylinder. Freezing rates in the casting were measured by means of thermocouples made from 30-gauge iron and constantan wire. One leg was dipped in molten sodium chloride before use to provide a coating to prevent electrical short circuits through the molten metal. The time interval between liquidus temperature [assumed 1115°F. (602°C.)] and the solidus temperature [assumed 750°F. (399°C.)] for a casting was measured by a stop clock. For the cast-iron mold it amounted to about 6 sec., for the cold sand mold, about 1½ min., and for the hot sand mold, about 2½ min. These freezing times are of the same order of magnitude as those encountered in permanent mold and green-sand castings of similar cross section. After a number of measurements had shown no large variation in cooling rates, the use of thermocouples was discontinued.

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* Nominal composition Permanente No. 7 refining flux KCl, 52.5 per cent; $MgCl_2$, 40 per cent; $BaCl_2$, 6 per cent; CaF_2, 1.5 per cent.

† Nominal composition Permanente No. 21 covering flux KCl, 34 per cent; $MgCl_2$, 42 per cent; CaF_2, 14 per cent; MgO, 10 per cent.

The sprue was cut from the casting with a saw. Then the casting was cut on a high-speed cutting wheel into three pieces, as shown in Fig. 3. The center piece was solution-heat-treated in a salt-bath furnace for 16 hr. at 760° to 770°F. (404° to 410°C.) and the bottom piece for 5 hr. only. After solution heat-treatment, the specimens were cooled in air, a thin slice was removed from the surface by the cutting wheel, and the new surface was polished, etched and examined.

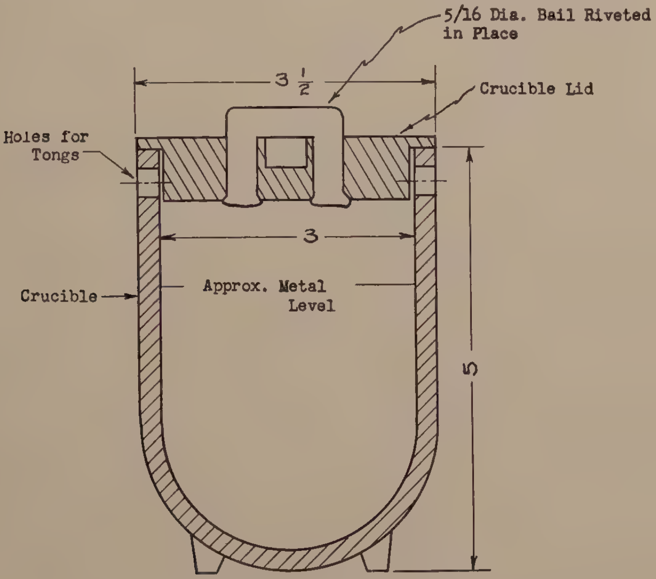

FIG. 1.—IRON CRUCIBLE, CAPACITY ABOUT ONE POUND.

When particular experiments call for deviation from this standard procedure, the deviation is described at the proper place in the text.

GRAIN-SIZE DETERMINATION

The grains of the metal as cast were dendritic and grain boundaries were difficult to recognize. After standard solution heat-treatment followed by air cooling, the grain boundaries stand out sharply. For this reason it is the usual practice to count grains only after full solution heat-treatment, and this practice was adopted. The response to heat-treatment was followed by observing the disappear-

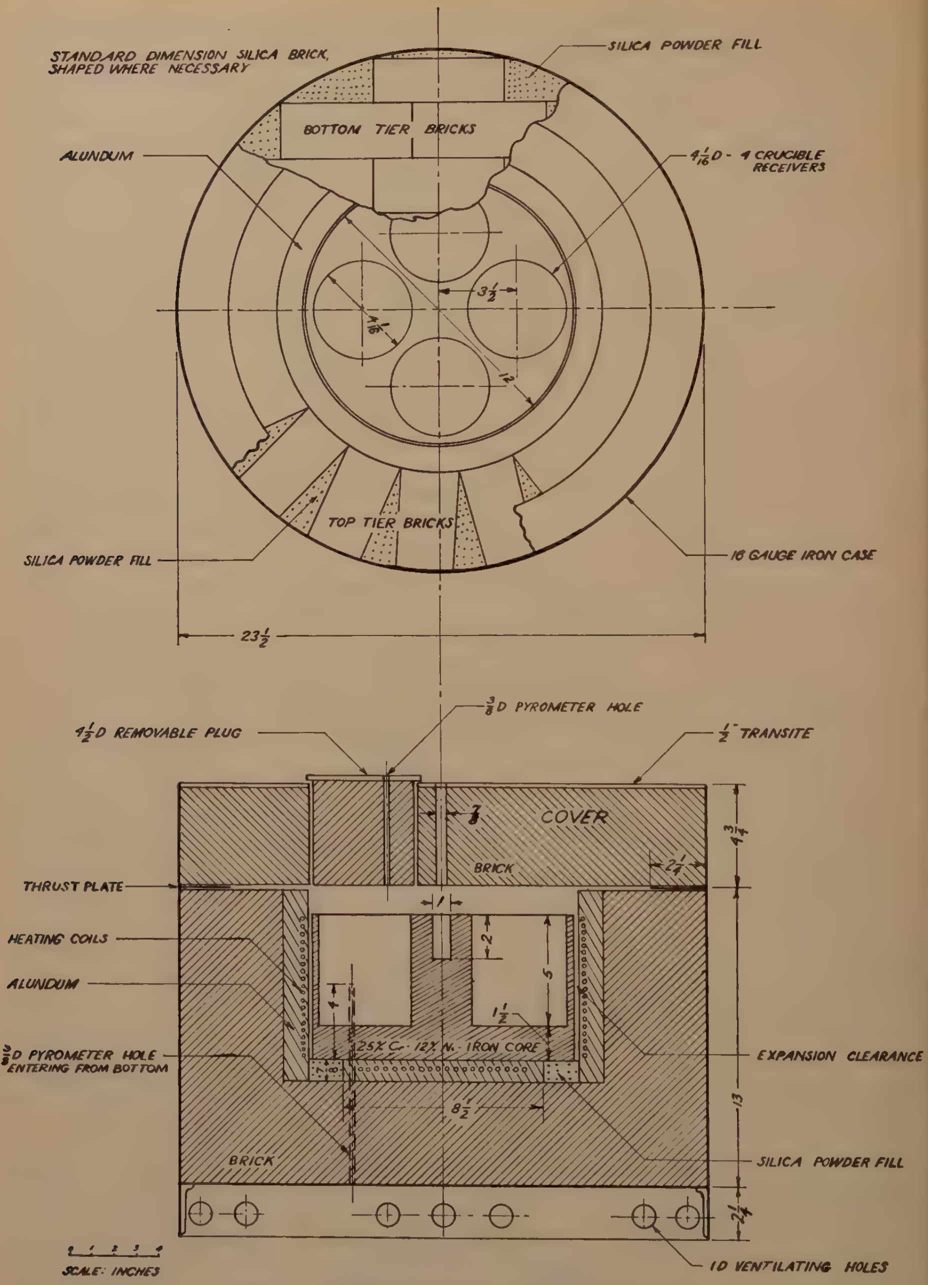

FIG. 2.—SUPERHEAT AND CASTING FURNACES.

ance of beta particles at shorter times of solution heat-treatment.

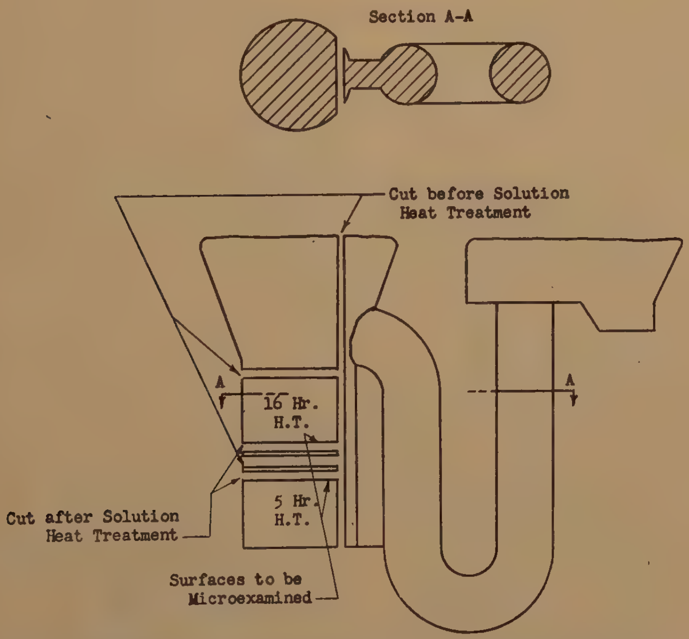
Section A-A
Cut before Solution Heat Treatment
A
16 Hr. H.T.
5 Hr. H.T.
A
Cut after Solution Heat Treatment
Surfaces to be Microexamined

FIG. 3.—METHOD OF SECTIONING CASTING FOR MICROSCOPIC EXAMINATION.

Various methods of grain-size determination were tried; among them: counting grains within a measured circular area projected on a ground-glass screen; comparison with transparent photographs of the A.S.T.M. austenitic grain-size standards; use of the standard austenitic grain-size eyepiece; and intercept methods.

The following method was selected because a large number of grains is counted and results can be reproduced closely by different observers. By means of a traveling stage, the sample is moved so that the cross hairs of the eyepiece traverse a square approximately 3 mm. on an edge about the center of the section. The number of grains traversed is counted so that grains intersected per millimeter are determined. This can be converted to grains per square millimeter by squaring and multiplying by a constant. This constant can be found by traversing a number of samples whose grains per square millimeter have already been found by counting grains in circular fields projected on a ground-glass screen. Consistent results were obtained.

EFFECT OF TIME AND TEMPERATURE OF SUPERHEAT ON GRAIN SIZE

In contradiction to published results for electrolytic magnesium, full grain refinement in carbothermic A.S.T.M. No. 17 alloy can be obtained at temperatures as low as 1400°F. (760°C.). With our heating and cooling cycle, if sufficient time is allowed at superheat temperature, the resulting grain size is virtually independent of temperature above 1400°F. (760°C.) to the highest temperature tested, 1800°F. (982°C.), as shown in Table 1. The values given are averages of large numbers of observations. In spite of the carefully controlled experimental conditions, individual observations deviated considerably from the average, although nearly all of them agreed with the average within a factor of two. Typical data are shown in Table 2.

TABLE 1.—*Grain Size as a Function of Superheat Temperature*
CASTING TEMPERATURE 1400°F. (760°C.)

Temperature of Superheat,[a] Deg. F.	Average Grain Size, Grains per Square Millimeter			
	Cast-iron Mold 360°F. (182°C.)	Cold Sand Mold 75°F. (24°C.)	Hot Sand Mold 360°F. (182°C.)	Number of Observations
Unsuperheated[b]	94	8	9	10
1400	615	105	122	40
1500	455	157	117	44
1600	402	153	114	47
1700	320	131	108	20
1800	360	91	34	2

[a] All samples were held a sufficient time at superheat temperature to obtain maximum grain refinement.

[b] Two minutes at 1400°F. (760°C.).

TABLE 2.—*Typical Data Showing Effect on Grain Size of Time of Holding Unsuperheated Metal at* 1400°F. (760°C.)
CASTING TEMPERATURE 1400°F.

Heat No.	Time at 1400°F., Min.	Grain Size, Grains per Square Millimeter		
		Cast-iron Mold 360°F. (182°C.)	Cold Sand Mold 75°F. (24°C.)	Hot Sand Mold 360°F. (182°C.)
83	2	70	6	10
85	2	199	12	22
83	15	265	14	45
84	15	350	51	112
85	15	490	112	109
86	15	135	21	22
83	60	1120	92	138
84	60	1040	113	109
85	60	485	119	159
86	60	770	159	103
95	60	605	87	174
96	60	620	127	114
97	60	357	76	175
83	240	586	58	112
85	240	435	79	84
95	240	904	158	138
96	240	1030	142	149

The time required to obtain this refinement was about one hour at 1400°F. (760°C.), 15 min. at 1500°F. (816°C.), while at higher temperatures it was attained during the heating and cooling cycle, without the necessity of holding at superheat temperature. Fig. 4 shows the effect of time of holding at 1400°F. (760°C.).

A limited amount of work was done at temperatures below 1400°F. (760°C.). Unsuperheated metal held at 1300°F. (704°C.) and 1350°F. (732°C.) experiences a gradual grain refinement. Metal that has been superheated and cooled to these temperatures gradually coarsens. Grain sizes obtained were intermediate between those obtained with unsuperheated metal and with metal superheated to full grain refinement.

EFFECT OF OTHER VARIABLES ON GRAIN SIZE

The procedure described under experimental methods was varied in certain respects in order to determine possible effects on grain refinement.

The rate of cooling from superheat to casting temperature was varied from 100°F. to 10°F. per min. without noticeably affecting the grain size.

Identical castings made in close succession from the same crucible proved to have the same grain size. This indicates that the nucleating constituent, whatever its nature, does not segregate in the bottom or top of the crucible by gravity.

It was found that when two of the four iron crucibles used in a single melt were replaced by graphite crucibles, and all four were superheated at 1600°F. (871°C.) by the methods described, the grain size of the castings poured from the iron crucibles were 20 to 30 per cent finer than those from the graphite.

Some superheating was done in 50-lb. iron pots with castings poured in green sand. Under these conditions, grain refinement occurred at temperatures as low as 1400°F. (760°C.) and the final grain size depended only a little on the temperature of superheat above 1400°F. Thus the results obtained using the one pound laboratory crucibles and baked sand molds appear to be applicable to large pots and green-sand molds.

DISCUSSION OF RESULTS

Carbothermic A.S.T.M. No. 17 magnesium alloy experiences grain refinement at temperatures considerably lower than those reported for alloys of electrolytic origin. This indicates that it contains some constituent not present in electrolytic metal. The grain size of electrolytic metal may be refined at equally low temperatures if carboniferous gases are bubbled through it.[5] Formation of a carbide may be responsible for this. A carbide is a likely constituent of carbothermic but not of electrolytic metal. It has been found at this laboratory that the gases will also refine carbothermic metal, while mechanical agitation will refine either carbothermic or electrolytic alloys at comparatively low temperatures. This will be discussed in detail in a subsequent paper.[7]

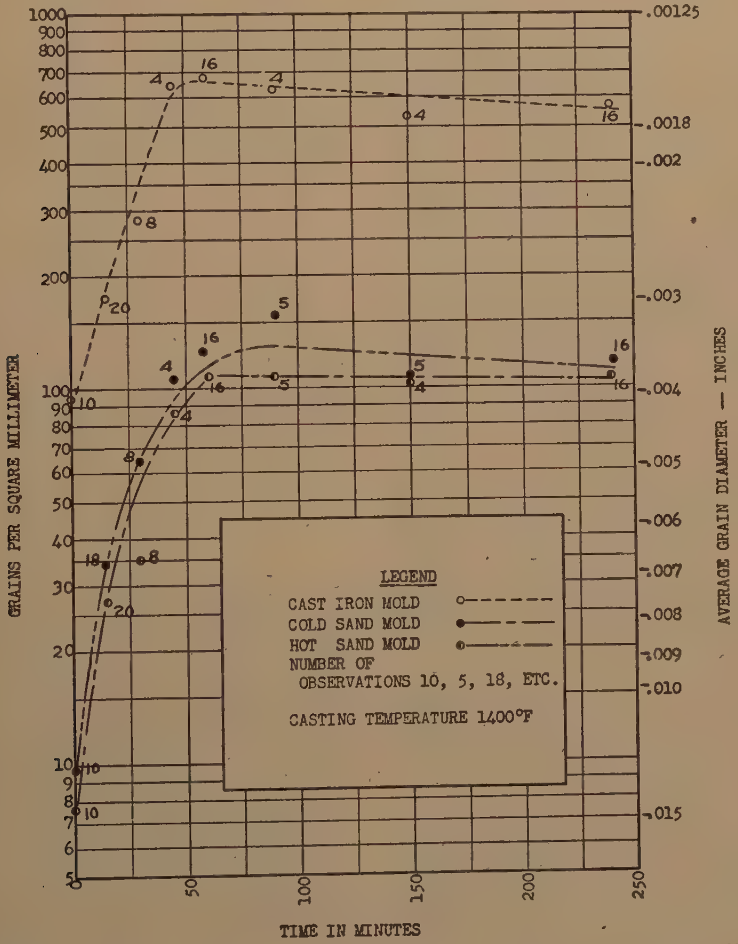

FIG. 4.—EFFECT OF TIME AT 1400°F. ON GRAIN SIZE OF UNSUPERHEATED CARBOTHERMIC A.S.T.M. No. 17 ALLOY.

It is asserted in German literature[2] that finer grains are obtained by increasing the temperature of superheat. We have found, on the contrary, that the average grain size obtained under our conditions is almost independent of temperature between 1400° and 1800°F. (760° and 982°C.), the highest temperature yielding slightly coarser grains. While this result has been obtained for carbothermic magnesium, it is possibly also true for electrolytic, there being no published quantitative data on this subject. As expected, grain refinement occurs more rapidly at higher temperatures.

It must be admitted that the nature of the nucleating constituent has not been established.* Although there is some evidence that carbides may play this role, grain refinement may be secured in electrolytic magnesium alloys by either superheating or stirring under conditions where there is no reason to suspect the presence of carbon.

SUMMARY

1. Carbothermic A.S.T.M. No. 17 magnesium alloy experiences full grain refinement at temperatures as low as 1400°F. (760°C.). This is considerably lower than the temperatures reported to be necessary for alloys prepared from electrolytic magnesium.

2. When held at 1300° or 1350°F. (704° or 732°C.) the unsuperheated alloy experiences incomplete grain refinement while the superheated alloy coarsens to some extent.

3. The grain size obtained is virtually independent of superheat temperature provided sufficient time of superheating is allowed.

4. The time required for full grain refinement of carbothermic A.S.T.M. No. 17 alloy is one hour at 1400°F. (760°C.) and much less at higher temperatures.

5. It is suggested that carbothermic magnesium contains some constituent, perhaps a carbide, that is responsible for its low temperature of grain refinement.

6. Other processes for securing grain refinement at low temperatures will be discussed in a subsequent paper.[7]

ACKNOWLEDGMENT

The authors are grateful to Dr. Robert I. Jaffee and to Simon A. Prussin, who supervised much of the metallographic work; to Susan Richardson and Helen McReynolds for metallography and to Chester Cromwell, Daniel M. Belmont, and Paul Travis for experimental work in casting.

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* For discussion of this subject see reference 6.

Grain Refinement of Magnesium Alloys without Superheating

By Ralph Hultgren,* Member and David W. Mitchell,† Junior Member A.I.M.E.

(New York Meeting, February 1945)

MAGNESIUM alloys usually are superheated before casting in order to ensure fineness of grain. Superheat temperatures in common use range from 1600° to 1700°F.; the casting temperature, which depends upon the mold shape, is usually 200° to 300°F. lower. The process of superheating requires considerable time and seriously shortens the life of the iron pots used.

Recently it has been reported[1] that if acetylene, carbon dioxide or natural gas is bubbled through molten electrolytic A.S.T.M. No. 4 alloy at 1400°F. for 5 min., grain refinement equivalent to that of superheating will take place. Addition of certain solids such as graphite or aluminum carbide accomplishes the same results.[2] As will be shown in this paper, it is possible to achieve grain refinement in magnesium casting alloys at low temperatures by mechanical stirring of the molten metal for a short time. This process was developed in the course of research work, supervised by the War Metallurgy Committee under the "Restricted" Project NRC-550, for the Office of Production Research and Development of the War Production Board. This paper, based on that work, has been released for publication by the O.P.R.D.

MATERIALS AND METHODS

The alloys studied were the most common American sand-casting alloys designated as No. 4 and No. 17 by the American Society for Testing Materials. The magnesium used in these alloys was of both carbothermic[3] and electrolytic[4] origin. Chemical analyses supplied by the producers are shown in Table 1.

Each heat consisted of approximately 5 lb. of alloy melted in a Tercod crucible. It was refined by fluxing with Permanente No. 7* refining flux at 1300° to 1350°F. After cooling to 1200° to 1250°F., portions of approximately one pound each were ladled into iron crucibles contained in an electric furnace at about 1250°F. The molten metal was covered with Permanente No. 21† covering flux and then heated to the temperature to be investigated. Normally each of the four portions was given a different treatment. In a typical case one portion was stirred vigorously for 5 min., acetylene gas was passed through a second portion for 5 min., a third portion was superheated to 1600°F. for 15 min., then cooled to casting temperature, and the fourth was held for 5 min. at the temperature of stirring or gassing without other treatment. Each portion was then cast into one-inch diameter cylinders in three "nonturbulent" molds of identical shape. One mold was made of cast iron and the other two of baked sand. The cast-iron mold and one of the baked sand molds were heated to 360°F., the other baked sand mold was at room temperature. The freezing times in these molds were

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† Lecturer in Metallurgy, University of California.

[1] References are at the end of the paper.

* Nominal composition Permanente No. 7 refining flux KCl, 52.5 per cent; $MgCl_2$, 40; $BaCl_2$, 6; CaF_2, 1.5.

† Nominal composition Permanente No. 21 covering flux KCl, 34 per cent; $MgCl_2$, 42; CaF_2, 14; MgO, 10.

about 6 sec. for the cast iron, 1½ min. for the cold baked sand, and 2½ min. for the hot baked sand when the casting temperature was 1400°F. The one-inch cylindrical sections were cut from the sprue and given a complete solution heat-treatment. A fresh surface was then cut and the grain size determined. For details of apparatus and procedure see a previous paper.[5]

TABLE 1.—*Compositions of Alloys*

A.S.T.M. No.	Origin	Producer	Al, Per Cent	Zn, Per Cent	Mn, Per Cent	Si, Max.	Cu, Max.	Ni, Max.	Pb, Max.	Fe, Max.	Ca, Per Cent
17	Carbothermic	Permanente	8.62	2.07	0.49	0.2	0.04	0.005			
17	Electrolytic	Dow	9.1	1.8	0.30	0.01	0.01	0.001			
17	Electrolytic	Basic	9.3	2.3	0.21	0.02	0.01	0.001	0.001	0.02	
4	Carbothermic	Permanente	5.66	2.67	0.38	0.01	0.001		0.01	0.003	0.01

RESULTS

Carbothermic No. 17 alloy was treated at 1400°F. by bubbling of natural gas or acetylene or by mechanical agitation. The results were compared with those obtained by superheating at 1600°F. for 15 min. and with untreated metal held at 1400°F. for 5 min. It was found that the bubbling with natural gas or acetylene produced grain refinement approximately equal to that obtained by superheating, in agreement with results reported for No. 4 alloy.[1] Stirring, which was done by hand with an iron rod, produced equally fine grains. It was later found that more vigorous stirring caused increased grain refinement. Average results obtained for a number of observations are shown in Table 2. Individual observations of grain size deviated as much as a factor of 2 from the average.

TABLE 2.—*Grain Size of A.S.T.M. No. 17 Alloy after Treating 5 Minutes at 1400°F. Compared with Superheating at 1600°F. for 15 Minutes*
CASTING TEMPERATURE 1400°F.[a]

Mold	Treatment				
	Acetylene, Grains per Sq. Mm.	Natural Gas, Grains per Sq. Mm.	Stirring, Grains per Sq. Mm.	Superheated, Grains per Sq. Mm.	Untreated, Grains per Sq. Mm.
Cast iron..	(4) 242	(3) 393	(15) 284	(7) 357	(11) 156
Cold sand.	(4) 115	(3) 205	(7) 206	(13) 147	(16) 15
Hot sand..	(4) 128	(3) 117	(15) 144	(6) 128	(10) 11

[a] Figures in parenthesis indicate number of observations used in calculating averages.
"Average grain diameter" equals

$$\frac{1}{\sqrt{\text{no. of grains per unit area}}}$$

Further investigation showed that most of the grain refinement occurred during the first minute of stirring at 1400°F. Table 3 shows the effect of time of stirring.

TABLE 3.—*Effect of Time of Stirring on Grain Size of Carbothermic No. 17 Alloy*
AVERAGES OF FOUR OBSERVATIONS
Stirring Temperature 1400°F.
Casting Temperature 1400°F.
Baked Sand Mold at Room Temperature

TIME OF STIRRING, MIN.	GRAINS PER SQ. MM.
0	4
1	112
2	130
4	122
5	100

A.S.T.M. No. 17 alloy made from electrolytic metal was next studied to determine whether stirring at 1400°F. caused grain refinement. Ingots obtained from Dow Chemical Co. (Dowmetal C) and from Basic Magnesium Corporation both showed the same phenomenon in approximately the same degree as carbothermic metal. In Table 4, results obtained with electrolytic metal are shown.

The effect of the material of the pot and the stirring rod was next studied. Two portions from each heat were stirred at 1400°F. for 5 min. in graphite crucibles with graphite rods while two others were stirred in iron crucibles with iron rods. All were cast into identical baked sand molds at room temperature. No appreciable differences in grain size were found. The average of observations for metal treated in the iron crucibles was 218 grains per sq. mm., which compares with 246 grains per sq. mm. for that treated in the graphite crucibles. Carbothermic No. 17 alloy, which had been melted in an iron pot instead of a Tercod crucible, and had not come into contact with carbon while molten, also experienced grain refinement on stirring in iron crucibles.

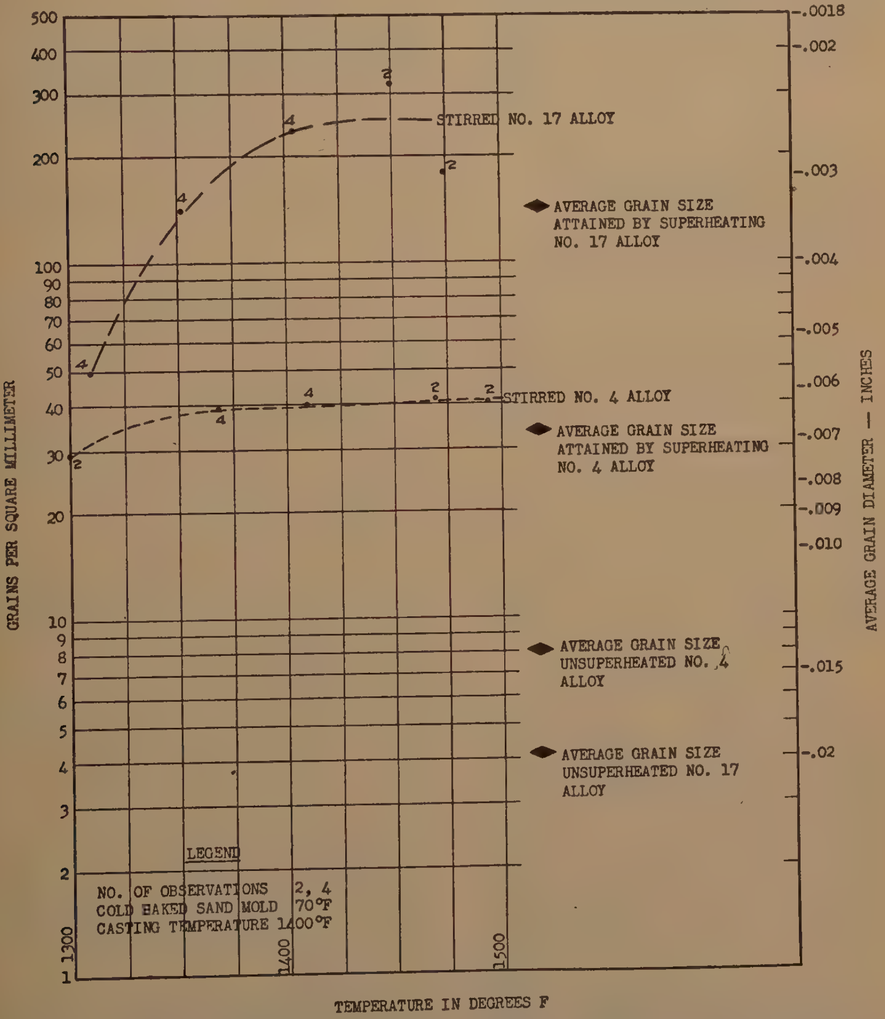

FIG. 1.—EFFECT OF TEMPERATURE OF STIRRING ON GRAIN SIZE OF MAGNESIUM ALLOYS. Each alloy was stirred vigorously for 5 minutes at indicated temperature.

Carbothermic No. 4 alloy experienced grain refinement approximately equivalent to that obtained with superheating (Fig. 1).

When stirring was done at temperatures above 1400°F. the tendency to burn was greater and the final grain size obtained was no finer. Above 1500°F. stirring became impossible without protection from air and experiments were not carried out. Somewhat below 1400°F. the grain refinement obtained upon stirring for 5 min. began to decrease as shown in Fig. 1.

TABLE 4.—*Effect of Stirring on Grain Size of Electrolytic No.* 17 *Alloy*
AVERAGED OBSERVATIONS
Stirring Temperature 1400°F.
Casting Temperature 1400°F.
Stirring Time, 5 Minutes
Baked Sand Mold at Room Temperature

Producer	Grains per Sq. Mm.		
	Stirred	Untreated	Superheated
Dow	260	28	154
Basic	201	20	108

After refining by stirring, flux and other inclusions may be allowed to settle out just as in unstirred metal. Flux and oxide inclusions were absent in specimens of metal refined by stirring and examined microscopically.

DISCUSSION OF RESULTS

Several methods of obtaining grain refinement without superheating of magnesium casting alloys are available. Each of them promises possibilities of commercial application. The question as to whether bubbling of gas, addition of solid agents, mechanical agitation, or superheating is the best is a technological one that can be settled only by plant-scale operation and cost analysis. Each of these methods has its disadvantages. The method suggested in this paper, stirring, has not been tested on a large scale and possibly there may be difficulty in securing the requisite intensity of agitation.

The cause of grain refinement in magnesium alloys remains unexplained. Carbothermic metal will refine at 1400°F. if time is allowed.[8] It might then be considered that stirring merely increases the rate of some reaction, whatever it may be. However, electrolytic metal, according to all reports (p. 322 of ref. 4, also ref. 6), does not experience grain refinement except at considerably higher temperatures, while its grain refinement on stirring at 1400°F. is equal to that of carbothermic metal.

Grain refinement by stirring does not appear to be due to a reaction with the crucible or stirring rod, since the same result is obtained when these are made of graphite as when they are made of iron.

SUMMARY

1. Grain refinement of A.S.T.M. alloys Nos. 17 and 4 may be obtained without superheating if they are stirred vigorously at 1400°F.

2. Electrolytic and carbothermic magnesium alloys both experience full grain refinement on stirring.

3. Most of the grain refinement occurs in the first minute of vigorous stirring in small one-pound crucibles.

4. After stirring, the metal may be allowed to stand at 1400°F. to prevent flux and oxide inclusions.

5. Increasing the temperature of stirring above 1400°F. does not increase the degree of grain refinement while burning of the metal becomes a serious problem. At lower temperatures the degree of refinement decreases.

6. Stirring in a graphite crucible with a graphite rod gives the same grain refinement as stirring in an iron crucible with an iron rod.

7. Bubbling of acetylene or natural gas through molten No. 17 alloy refines its grain in agreement with results reported for No. 4 alloy.

ACKNOWLEDGMENT

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A Study of Factors Influencing Grain Size in Magnesium Alloys and a Carbon Inoculation Method for Grain Refinement*

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(New York Meeting, February 1945)

Magnesium, it is now generally realized, differs in some important aspects from most other structural metals, not excepting even its close neighbors, the aluminum-base alloys. This is particularly true with respect to the effects of elevated temperatures on the two light metals when in the molten state. Aluminum, on the one hand, should not be raised above its melting point any higher than is absolutely necessary if one is to avoid danger of gas absorption and a tendency toward grain growth in the resultant casting.[1] Magnesium alloys, in sharp contrast, actually benefit by being heated to temperatures considerably above their melting point. It is a commonly accepted practice to establish the desired fine grain in the industrial magnesium alloys of the aluminum-bearing group by raising the temperature of the melt after the refining treatment to some 250°C (482°F.) above the melting range.

To recall briefly the typical practice for magnesium alloys, the molten metal is refined by fluxing at about 730°C. (1350°F.), and after the melt has been covered with a suitable flux, the temperature is raised to between 870°C. (1600°F.) and 930°C. (1700°F.). It is then cooled as quickly as possible to the casting temperature. This superheating, as it is called, results in a fine-grained cast metal structure which has superior mechanical properties, enhanced amenability to solution heat-treatment, and better machinability than cast metal that has not been superheated. The minimum temperature of superheating varies to some extent with the composition of the alloys to be treated and usually increases with the percentage of magnesium in alloys containing the same constituent metals.[2] It should be noted that the grain-refining effect of superheating is markedly apparent only in connection with the alloys containing aluminum as an alloying constituent—the binary alloy containing 1.5 per cent manganese, for example, is not refined in grain to any noticeable extent by a superheating effort. While the phenomenon of superheating is well known in the magnesium industry, the mechanism of the process has remained a mystery. During the superheating cycle something occurs that forces a fine grain upon the solidifying metal. The process has been controlled in an empirical manner, and occasionally, especially on large-scale melts, and for no apparent cause, no grain refinement is obtained from a superheating treatment.

Only a few papers of importance have been published on the subject. Of these, one of the most helpful is the paper by Achenbach, Nipper and Piwowarski,[3] which gives considerable data concerning the effect of superheating on various properties such as fluidity, shrinkage and hot crack

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[1] References are at the end of the paper.

formation, as well as grain size, and a discussion without any definite conclusions on the theoretical aspects of superheating. A short article by Murphy, Wells and Payne[4] describes the influence of superheating observed under commercial sand-casting foundry conditions. The investigations of grain-size phenomena by the War Metallurgy Committee for the War Production Board give the most recent scientific contributions on control of grain size.[5]

It is known that castings made from melts containing considerable proportions of wrought and machine scrap characteristically possess a finer grain structure than the same casting made from virgin metal. Also, it is supposed that continued remelting sometimes has beneficial effects.

It has been generally considered that the grain size of any cast metal is dependent upon one or more of the following factors: (1) mold conditions such as temperatures and surface coatings; (2) casting temperatures of the metal poured; (3) mechanical conditions such as turbulence during pouroff, mechanical vibration of the mold or turbulence due to gas evolution; (4) surface tension of the solid and liquid phases present during solidification; (5) viscosity of the molten metal; (6) the presence of grain-forming nuclei. Other factors, dependent upon the nature of the alloy, such as energy of crystallization, latent heat of fusion and solidification range, may influence grain size.

The phenomenon of grain refinement of magnesium-aluminum alloys by superheating would seem almost certainly a matter of nucleation. In general, two fundamentally different types of nuclei may be present in a molten metal and may be characteristically termed (1) kindred nuclei and (2) foreign nuclei. Kindred nuclei we consider to be metal anisotropic residues that exist in melts that otherwise are isotropic and that should be expected to be produced in very large numbers if the melt supercools below its melting point.[6] The formation of a very large number of nuclei would result in a correspondingly large number of crystals, and consequently a fine grain size. Such undercooling, with the resultant formation of large numbers of nuclei, may therefore be an important cause of fine grain formation of some alloys. However, observations made by Achenbach, Nipper and Piwowarski[3] showed that while nonsuperheated melts of magnesium alloys showed some slight undercooling effects, superheated melts did not show such effects. Consequently, these studies would not appear to offer much basis for believing that the grain-refining effects of the superheating of magnesium alloys are due to supercooling. Foreign nuclei may be taken to include all the substances present in the melt that are not present in the ideally "pure" melt and are not in solution. These foreign nuclei can be generally expected to promote the formation of solid material of the particular crystal system to which they themselves belong. If such nuclei are purposely added to melts, the process is referred to as "inoculation" and in any grain-refinement process in which such nuclei are added the term "inoculant" is given to the material that acts as centers of crystallization. Foreign material may be present, of course, in a melt without influencing the crystallization process at all, and the principal refinement effects are generally confined to certain types of nuclei for specific alloy systems.

The following points should be given consideration in developing any theory seeking to explain the superheating phenomena of magnesium alloys: (1) the grain-refining effect is peculiar to the alloys of magnesium that contain aluminum; (2) the grain-refining effect is not permanent and tends to be lost when the metal is remelted; (3) on some alloys the grain-refining effect tends to be lost if the superheated melt is allowed to stand for a period of time at a temperature above the melting range; (4) the grain-refining effect is partially lost as a superheated melt is cooled; (5) the grain-refining effect may be lost to some extent if a maximum temperature in the region of 900°C. is exceeded or if the melt is held at normal superheating temperatures for excessively long times; (6) instances occur at more or less frequent intervals where superheating efforts with large melts result in the apparent failure to effect any grain refinement, or may even result in the production of ingots with a grain size larger than can be deliberately produced by any known procedure.

No theory has been put forward to explain adequately all these known facts. It appears logical that there are two principal explanations to be considered; either that grain refinement by superheating is due to the absence of foreign nuclei and subsequent supercooling effect; or that the grain refinement is due to the production of cloudlike dispersions of foreign nuclei with no undercooling involved.

The most widely supported theory[7] at present is that some material that is too large in particle size at normal temperatures to serve as nuclei is taken into solution at the higher temperature, and reprecipitates to form fine nuclei during the cooling process. There are several strong points in favor of this theory:

1. The phenomenon is specific for certain magnesium alloys. If a foreign-nuclei-free melt and subsequent supercooling were responsible for the fine grain it would be expected that even magnesium itself and other magnesium alloys, aside from those containing aluminum, should be capable of being made nuclei free by heating to elevated temperatures and hence grain-refined by undercooling. This, however, does not occur.

2. The fact that the grain-refining effect, after being accomplished by superheating, deteriorates at temperatures below the superheating range would lend credence to the idea that these nuclei are again coalescing and are growing to their original form and becoming relatively ineffective.

3. A remelt of a previously superheated alloy does not possess the fine grain originally obtained in the initial casting unless the remelt is carried to a superheating temperature. This would indicate that coagulation of grain-forming nuclei may have taken place during the remelting process, and that carrying the melt to an elevated temperature after remelting is required in order to achieve redispersion.

The most attractive and simple suggestion that has yet been offered to explain these effects in magnesium-aluminum alloys assumes that certain impurities in normal melts of these alloys are capable of dissolving in the melt to an increasing extent at elevated temperatures. During the cooling of the melt from superheating temperature to casting temperature, minute crystals of the impurity concerned are precipitated from the melt as a cloudlike dispersion, each particle then acting as a center for crystallization. The thought is also advanced that the impurity concerned is an iron-containing compound, perhaps even an iron-aluminum compound, and therefore an almost unlimited supply of nuclei-forming material would be available under normal melting conditions.[8] If this latter premise is accepted, it should be expected that the superheating effect would be lost by a settling of the nuclei on standing at low temperatures. The effectiveness of beryllium in lowering the iron content of magnesium alloys, together with its grain-coarsening influence, might be taken as corroborative evidence of this conception.[9] However, we find no evidence in our investigation that iron or iron compounds affect grain refinement.

Regardless of the actual modus operandi of superheating, the benefits have been confirmed many times in general industrial practice, and the treatment is considered very important in the production of high-quality castings.

The use of superheating technique is claimed by British Patent 359425, having an application date of June 16, 1930. It is rather surprising that such a phenomenon has not received greater attention by research investigators over the period of intervening years. At the time the authors initiated their investigations, more than two years ago, some people believed that there was a great advantage in using fine-grained ingot to achieve a carryover of fine grain in the casting. This belief is supported by many of the phenomena encountered in superheating practice with magnesium-aluminum alloys but is not supported by some observed results, such as, for example, the comparatively fine grain that seems to be native at temperatures close to the liquidus. The authors noted in actual practice that on some heats an apparent tendency toward carryover existed but that this tendency was neither sufficiently pronounced nor dependably reproducible to remove the necessity for a re-superheating treatment. They also noted that large-scale heats of about 4000 lb. often failed to give a fine grain after superheating, even though cast in 5-lb. ingots.

TABLE 1.—*Typical Composition of Alloys*

Alloy No.	Chemical Composition, Per Cent								Total Other Impurities, Maximum Per Cent
	Aluminum	Zinc	Manganese	Silicon, Max.	Copper, Max.	Iron, Max.	Nickel, Max.	Lead, Max.	
A5	3.5– 5.0	0.2–0.5	0.15–0.4	0.10	0.02	0.02	0.001	0.001	0.30
A8	7.6– 8.5	0.2–0.6	0.2 –0.5	0.10	0.02	0.02	0.001	0.001	0.10
17	8.5– 9.5	1.7–2.3	0.13 (min.)	0.10	0.02	0.02	0.001	0.001	0.10
4	5.5– 6.5	2.7–3.3	0.18–0.5	0.10	0.02	0.02	0.001	0.001	0.10
2	9.4–10.6		0.13 (min.)	0.10	0.02	0.02	0.001	0.001	0.10
AZ91	9.5–10.5	0.2–0.6	0.2 –0.5	0.10	0.02	0.02	0.001	0.001	0.10

There were embarrassing moments when users of alloys reported that certain lots of production metal gave a coarser grain size after superheating than some lots of metal gave without superheating. All in all it was evident that another answer to the superheating phenomena needed to be found. It was further thought that a better knowledge of how and why the grain refinement occurred would make it possible to obtain grain refinement without superheating. This seemed heretical, but the prospect of controlling the grain size with certainty, and also of increasing the degree of grain refinement obtainable, seemed to justify the risk of a possibly futile attempt to solve a research endeavor of this nature while operating on a production-control basis.

This paper is a condensed report on the investigation of inherent grain size of magnesium alloys as related to casting temperatures from just above the melting range through superheating temperatures and the discovery of a treatment by which fine-grained metal results without superheating.* No new theory is offered for the original superheating process, but an explanation of the new process is offered for consideration, and it is felt by the authors that the achievements by the two processes are alike in nature and may satisfactorily be explained by the same theory.

EXPERIMENTAL PROCEDURE

The alloys used in this investigation were made from magnesium produced at Basic Magnesium, Incorporated, Henderson,

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* Patent Applications No. 533938 and No. 551422.

Nevada. As is generally known, this metal is produced by the electrolysis of anhydrous magnesium chloride, which is made by the high-temperature chlorination of magnesia. Some of the experimental melts were made from nonsuperheated alloy ingots produced in the refinery, and other melts were made in the metallurgical laboratory from commercially pure magnesium ingot and also from electrolytic cell metal. Alloying materials used included virgin aluminum ingot, high-grade electrolytic zinc, and manganous chloride. Typical analyses of the alloys studied are given in Table 1. All melts were made in steel crucibles heated in furnaces fired by propane gas, of such design that melts were not contaminated by the products of combustion. The majority of the melts were about 30 lb. in weight although a number of 60-lb. melts were made to obtain test bars for tests of mechanical properties. Most of the treatments tried were corroborated with 150-lb. heats and some methods were tried on production heats of 4000-lb. capacity. Test castings for grain-size determination were obtained by casting metal from a hand ladle into an open steel mold, which was preheated to approximately 200°C. (400°F.). The size of the test castings approximated about 6 by 2 by ¾-in. thick. Preliminary tests indicated that the small variations in size of these test specimens had no material effect on the grain size. In fact, early in the investigation it was recognized that the experimental procedure could be greatly simplified when it became evident that the casting temperature was by far the most important variable controlling the grain size of the metal poured from nonsuperheated melts. Temperatures of melts were determined

TABLE 2.—*Mean Results of Tests for Grain Size*[a]

Accumulated Time Element	Casting[b] Temperature		Average Grain Size[13] of Cast Ingots[c]									
			A5		A8		ASTM-17		ASTM-4		ASTM-2	
Minutes	Deg. C.	Deg. F.	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
60	650	1202	10.6	10.3	11.0	10.9	11.2	11.2	11.8	11.6	12.2	12.2
65	700	1292	9.4	9.2	10.0	10.0	10.0	9.8	9.8	9.6	10.4	10.5
70	750	1382	8.4	8.2	9.2	9.1	9.0	8.8	8.5	8.5	8.9	9.1
75	800	1472	7.5	7.5	8.5	8.5	8.4	8.4	8.0	8.0	8.0	8.0
SUPERHEATED MELTS												
60	650	1202	10.6	10.6	11.0	11.0	11.2	12.8	11.8	13.4	12.2	13.1
65	700	1292	9.4	10.7	10.0	11.6	10.0	13.0	9.8	13.7	10.4	13.9
70	750	1382	8.4	11.0	9.2	12.2	9.0	13.2	8.5	14.1	8.9	14.5
75	800	1472	7.5	11.3	8.5	12.8	8.4	13.5	8.0	14.4	8.0	14.8
90	850[d]	1562	8.8	11.8	9.9	13.1	10.0	13.8	11.2	14.7	10.5	14.9
105	900[d]	1652	12.0	12.0	12.5	12.5	13.6	13.6	14.9	14.9	15.0	15.0
CARBON-TREATED MELTS[e]												
60	650	1202	12.9	13.0	11.5	12.5	13.0	12.8	14.0	14.1	13.5	13.2
65	700	1292	12.0	13.4	12.0	12.6	12.2	13.0	14.4	14.5	13.0	14.1
70	750	1382	12.4	13.8	12.5	13.0	12.3	13.2	15.0	15.1	13.4	14.6
75	800	1472	14.0	14.0	13.5	13.5	13.4	13.4	15.7	15.7	14.9	14.9

[a] Test ingots cast in open permanent mold. The grain sizes of specimens cast in permanent mold were consistently from 1 to 2 grain sizes smaller than were the grain sizes of sand-cast specimens from similar metal.

[b] Time interval between casting temperatures approximately 5 minutes.

[c] Grain size of individual ingots measured by the microcomparison method to the nearest grain-size number and averaged to the nearest tenth.

[d] Metal held for 10 min. at these temperatures.

[e] Metal treated with carbon and refined at 760°C. and cooled down to 650°C.

by use of potentiometers and calibrated Chromel-Alumel couples, protected with steel tubes.

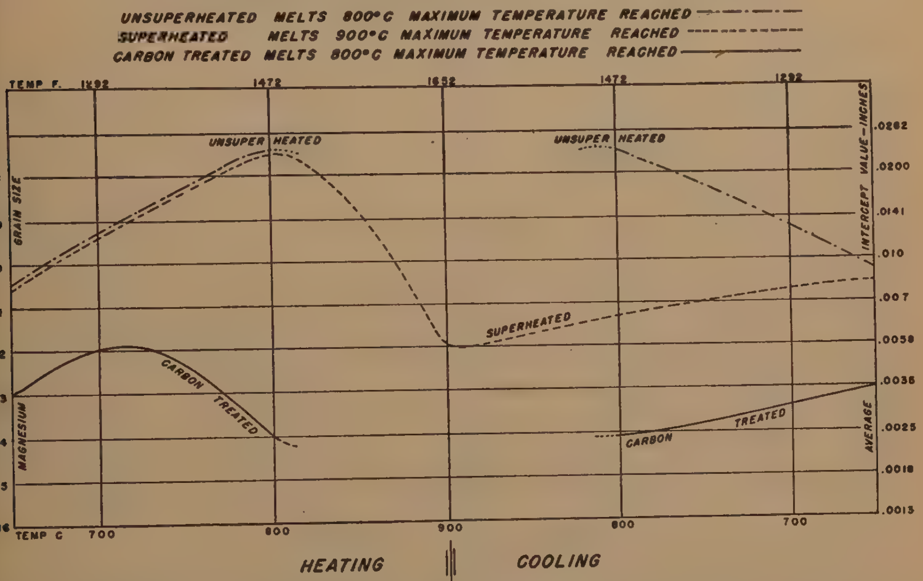

FIG. 1.—ANTICIPATED GRAIN SIZE VS. CASTING TEMPERATURE FOR MAGNESIUM ALLOY CONTAINING 5 PER CENT ALUMINUM.

Commercial melting and refining fluxes of the company's manufacture were used in melting and in refining. The refining was carried out at about 740°C. (1364°F.). The time cycles of the tests were standardized, dependent upon the test conditions, and are given in the notes of Table 2.

The special treatments given the alloys included, among others, the bubbling through the molten metal of various gases, including air, carbon dioxide, propane, flue gas, oxygen, nitrogen and ammonia, and the addition of solid carbon-containing materials such as magnesium carbonate, coal, peat, graphite, coke, lampblack and pitch. A few tests were also made to determine the effect of stirring on grain size in order to differentiate the effect of stirring from the combined effect of adding carbon in gaseous or solid forms and stirring.

The experiments consisted of two groups of tests. The first group included all tests made on melts of standard alloys to determine the characteristic grain size to be anticipated at various temperatures on cycles of heating, superheating, and cooling to just above the freezing point. Test samples were cast at the various temperatures in these ranges and grain size was determined by fracture of the as-cast samples as well as by microexamination of as-cast and solution-treated samples cut from the castings. The second group included all tests made on carbon-inoculated melts. These melts were not subjected to the regular superheating treatment and were corroborated by a number of 60-lb. melts for test bars. The carbon inoculation was usually accomplished by stirring pulverized carbon or carbonaceous material into the melt at approximately 750°C. (1380°F.), or by bubbling gas through the molten metal, and then raising the temperature to about 800°C. (1470°F.). The temperature was then decreased to about 650°C. (1200°F.) before the casting of test pieces was started. The temperature was then increased and samples were taken at temperature intervals of either 25° or 50°C. (77° or 122°F.) until a maximum temperature of 800°C. (1470°F.) was reached. The melt was then allowed to cool to 650°C. while samples were taken at similar intervals through the cooling cycle. The first heating step of this practice was followed in order to provide a sufficient time element to ensure an adequate cleansing of the melt and to simulate the time element of the refining step common to a normal foundry-floor practice.

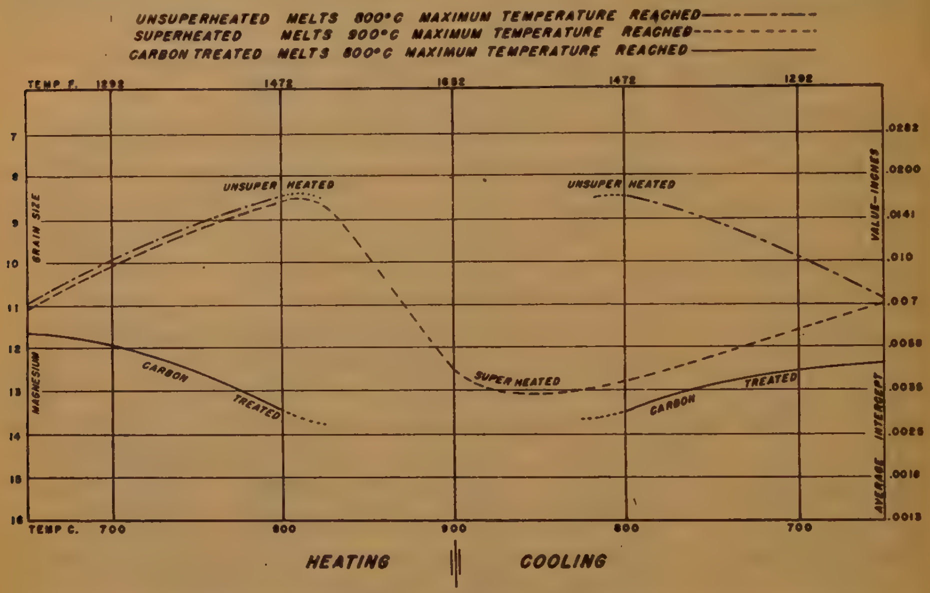

Fig. 2.—Anticipated grain size vs casting temperature for magnesium alloy A-8.

The system of magnesium grain-size designations used in this paper is described in a recent publication.[10] The procedure was briefly, as follows: The test castings were fractured after being sawed partly through from the bottom side, and were compared with standard fractures. One half of the sample was homogenized by solution treatment for 8 hr. at 380°C. (720°F.) and 16 hr. at 420°C. (890°F.). It was sensitized for etching by aging 2 hr. at 200°C. (390°F.). The as-cast structure was also examined to check for grain growth. Early in the investigation it was noted that the homogenizing of small prenumbered specimens resulted in erratic grain size but that when the specimens were cut from the prehomogenized halves of the test castings consistent results were obtained.

Experimental Results

The experimental data taken in this investigation are too extensive to permit presentation in this paper. Tabulations of mean results of grain-size measurements made on specimens from more than 2000 test castings poured from 110 experimental runs are given in Table 2. The results are also presented in chart form, for clarity, and show the mean of the grain-size determinations made on multiple runs of each alloy using different heats of metal. The ordinate axis on these charts is scaled, on the left to show magnesium grain-size numbers and on the right to show equivalent grain intercept values in inches. Magnesium grain-size numbers can be converted to A.S.T.M. austenitic grain-size numbers by subtracting 9. For example, a magnesium grain size of

8 is the same as minus one (−1) on the A.S.T.M. austenitic scale. The abscissa axis is scaled on the bottom to show centigrade degrees and on the top to show equivalent Fahrenheit degrees. The left halves of the charts cover the heating

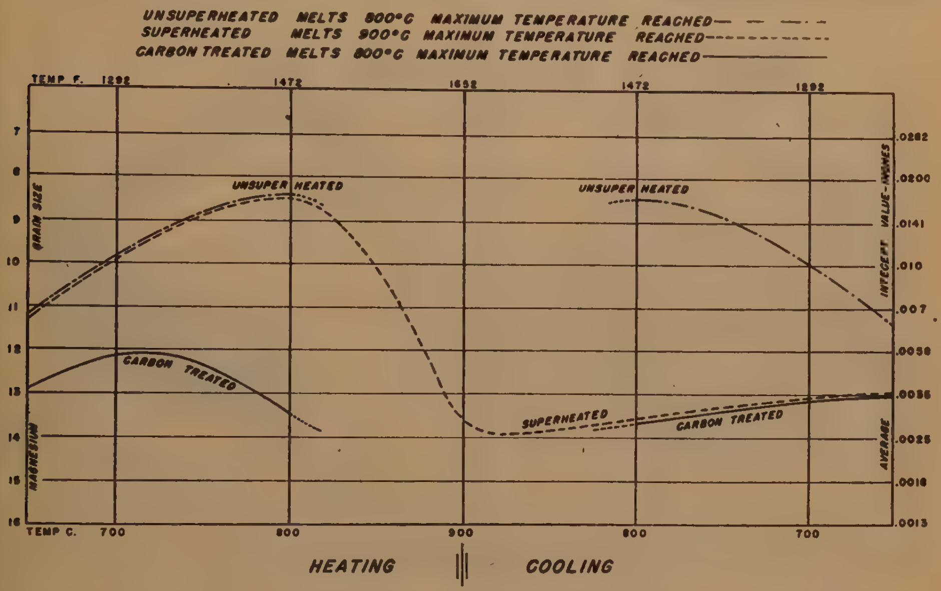

FIG. 3.—ANTICIPATED GRAIN SIZE VS. CASTING TEMPERATURE FOR MAGNESIUM ALLOY A.S.T.M. 17

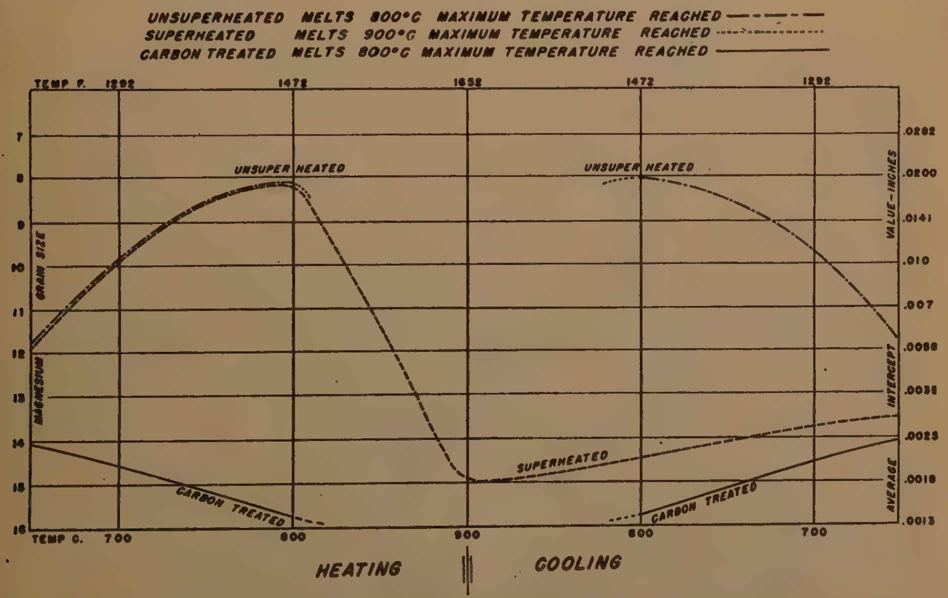

FIG. 4.—ANTICIPATED GRAIN SIZE VS. CASTING TEMPERATURE FOR MAGNESIUM ALLOY A.S.T.M. 4.

range whereas the right halves cover the cooling range.

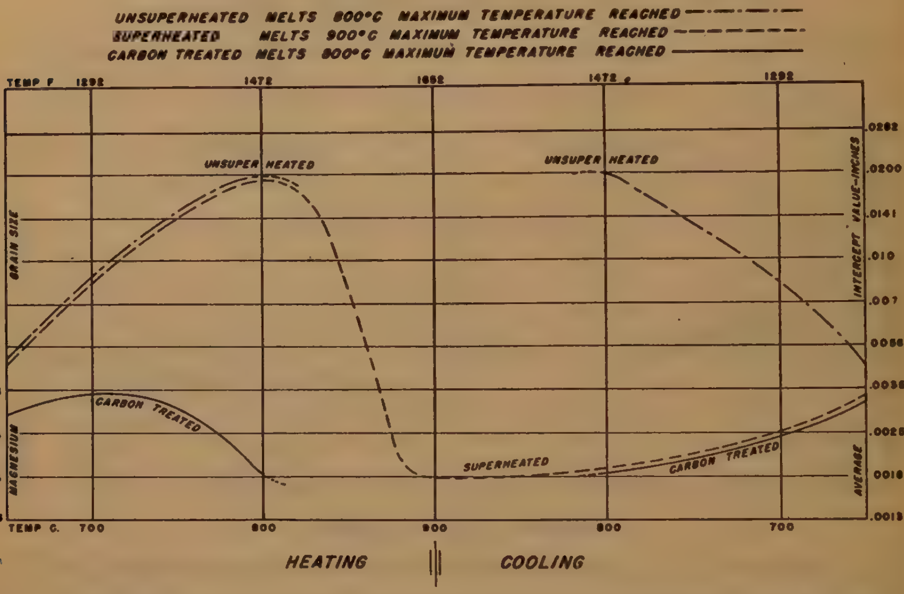

FIG. 5.—ANTICIPATED GRAIN SIZE VS. CASTING TEMPERATURE FOR MAGNESIUM ALLOY A.S.T.M. 2.

Fig. 1 shows the results of tests with an alloy that is similar to Elektron A5 and contains up to 5 per cent aluminum, 0.5 per cent zinc and 0.4 per cent manganese. This alloy was taken to represent the magnesium alloys of low aluminum content. The mean results of tests for nonsuperheated, superheated and carbon-treated melts are all shown on one chart, for ease of comparison, and as a consequence the continuity of the graphs for nonsuperheated and carbon-treated melts, which were not heated above 800°C., are interrupted by a gap in the superheating range. Thus, the graphs for the cooling phase of both nonsuperheated and carbon-treated melts have been displaced on the chart two spaces to the right, so that the effects of superheating could also be illustrated graphically on the same chart.

Figs. 2, 3, 4 and 5 show the results for alloys Elektron A8, A.S.T.M.-17, A.S.T.M.-4, and A.S.T.M.-2, respectively, and are constructed in the manner just described for the preparation of chart No. 1 (Fig. 1) for the Elektron A5 alloy. While the first five figures could be used as a basis for the discussion of results, Figs. 6 and 7 were prepared to give an over-all and a summary presentation, respectively, of the anticipated grain-size values for all alloys studied. Fig. 6 shows the full range of grain sizes without distinction as to alloy composition whereas Fig. 7 shows the individual expectancy values of grain sizes for each alloy.

Tables 3 to 7 show results of test on sand-cast test bars cast from carbon-treated melts of magnesium alloys A.S.T.M.-2, A.S.T.M.-4, A.S.T.M.-17, Elektron A8 and Elektron AZ91. Typical values from superheated melts of A.S.T.M. alloys 2, 4 and 17 published currently by commercial suppliers are given for comparison. The values the authors obtained from superheated Elektron alloy melts are also given for comparison with the carbon-treated A8 and AZ91 alloys.

The heat numbers showing a hyphen and the figure one (-1) identify heats that have been treated twice, using 0.1 per cent lampblack in each treatment. The other heats were treated only once with this amount of lampblack.

The results on a melt of Elektron-A5 type of alloy tested to determine the effect of stirring on the grain size are given in Table 8. Grain sizes are given for samples taken before and after stirring at the temperatures indicated.

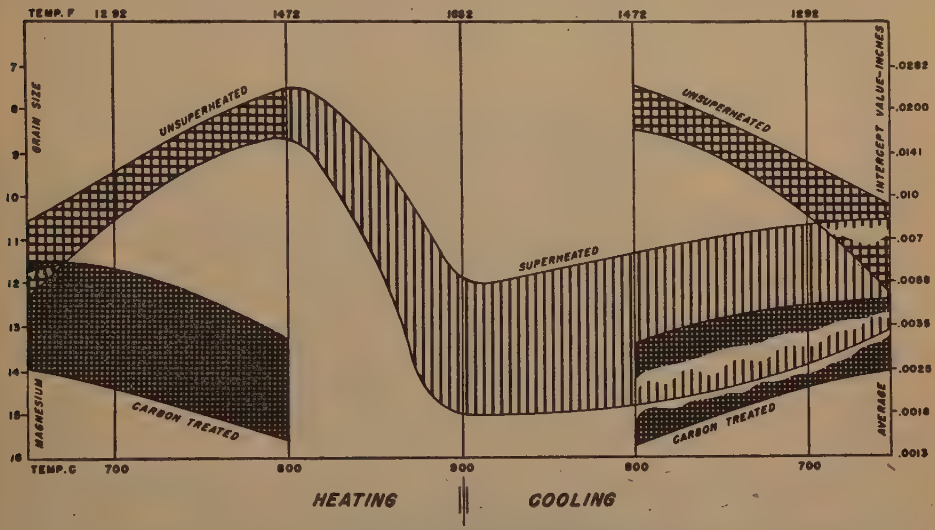

FIG. 6.—EXPECTANCY RANGE FOR COMMERCIAL MAGNESIUM-ALUMINUM ALLOYS RANGING FROM 4 TO 10 PER CENT ALUMINUM CONTENT.

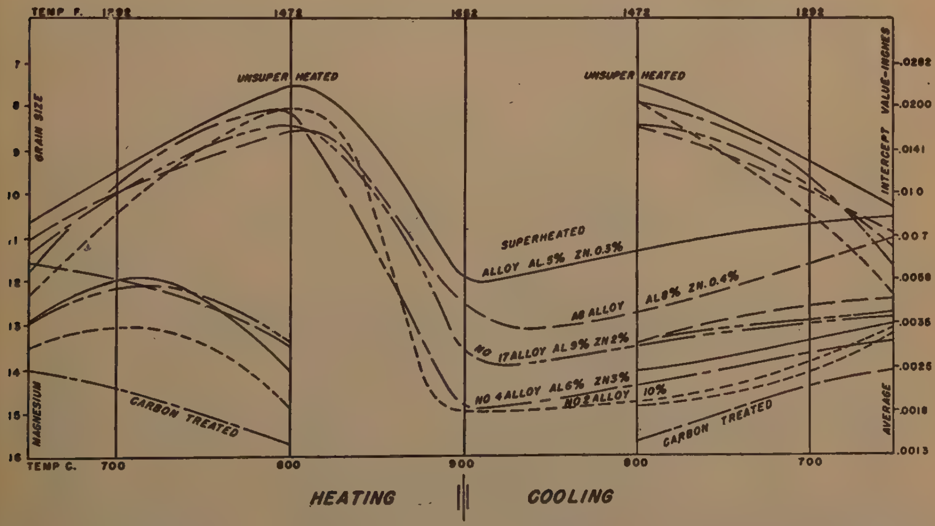

FIG. 7.—ANTICIPATED GRAIN SIZE VS. CASTING TEMPERATURE VARIATION WITH AMOUNT OF ALLOY AGENTS.

TABLE 3.—*Tensile Properties of Sand-cast Carbon-treated[a] A.S.T.M. No. 2 Alloy*

Heat No.	Condition	Tensile Strength, Lb. per Sq. In.			Yield Strength, Lb. per Sq. In.			Elongation, Per Cent in 2 In.			Magnesium Grain Size[10]
		Maximum	Minimum	Typical	Maximum	Minimum	Typical	Maximum	Minimum	Typical	
904	As cast	25,100	22,100	23,600	16,000	15,000	15,500	3.0	2	2.5	12.8
904-1		23,200	21,500	23,100	16,000	14,600	15,000	2.0	1	2.0	12.8
914		21,700	20,400	21,500	15,600	13,000	14,500	1.5	1	1.5	11.8
914-1		24,800	21,000	22,000	16,000	13,000	15,400	1.5	1.5	1.5	12.0
Average........		23,700	21,250	22,550	15,900	13,900	15,100	2.0	1.4	1.9	12.3
Published values			18,000	22,000		10,000	13,000		1	2	Superheated
904	Heat-treated (fused salt)	37,100	36,700	37,000	13,000	12,500	13,000	12.5	11.5	12	12.0
904-1		38,500	37,500	38,400	14,000	13,000	13,500	13.5	11	13	10.6
914		38,200	38,200	37,000	14,000	12,000	14,000	10	9	10	13.1
914-1		36,700	34,600	35,400	14,000	11,000	14,000	11.5	8.5	10.5	13.2
Average........		37,625	36,750	36,950	13,750	14,625	13,625	11.6	10	11.4	12.2
Published values			29,000	33,000		10,000	12,000		5	8	Superheated
904	Heat-treated aged	37,500	33,300	36,000	27,000	22,000	23,500	2	1	2	12.5
904-1		39,000	36,300	39,000	24,500	20,500	23,000	2.5	1	2	12.5
914		38,000	33,900	36,000	25,000	21,500	24,000	2	1	1.5	11.0
914-1		37,700	33,200	35,800	24,000	19,000	23,000	2	2	2	11.8
Average........		38,200	34,175	36,700	25,125	20,750	23,375	2.1	1.2	1.9	12.0
Published values			29,000	34,000		17,000	19,000			2	Superheated

[a] The metal was melted down in welded steel pots. It was refined with commercial refining flux at 740°C. When the melt had reached 760°C. it was treated with carbon and the metal was then allowed to drop back to casting temperature in a 10 to 20-min. period. Casting temperature was 710° to 720°C.

The mechanical results are based on rough-surfaced nonmachined test bars cast in high-permeability sand from 60-lb. melts. Commercial heat-treatment practices were followed throughout.

TABLE 4.—*Tensile Properties of Sand-cast Carbon-treated[a] A.S.T.M. No. 4 Alloy*

Heat No.	Condition	Tensile Strength, Lb. per Sq. In.			Yield Strength, Lb. per Sq. In.			Elongation, Per Cent in 2 In.			Magnesium Grain Size[10]
		Maximum	Minimum	Typical	Maximum	Minimum	Typical	Maximum	Minimum	Typical	
891	As cast	29,700	26,700	28,700	15,000	13,500	14,500	6.0	4.5	5.5	13.0
891		31,100	30,300	30,800	15,500	14,000	15,000	6.5	5	5.5	13.2
910		28,800	24,700	28,300	14,000	12,000	13,000	6.5	4	6.0	11.5
910-1		29,500	26,900	29,500	13,500	10,500	13,500	7.0	6	6.5	12.5
Average........		29,775	27,150	29,325	14,500	12,500	14,000	6.5	4.9	5.9	12.3
Published values			24,000	27,000		10,000	14,000		4	5	Superheated
891	Heat-treated (fused salt)	36,700	34,100	35,400	15,000	14,000	15,000	11	10	11	12.7
891		35,800	34,600	35,100	15,000	13,000	14,000	12	10	11.5	12.4
910		36,900	36,400	36,900	18,500	15,000	17,000	12.5	12	12.5	11.0
910-1		39,100	36,800	38,700	14,000	13,000	14,000	14.5	13	14.5	12.2
Average........		37,125	35,475	36,525	15,625	13,750	15,000	12.5	11	12.4	12.1
Published values			32,000	39,000		10,000	14,000		7	12	Superheated
891	Heat-treated aged	40,300	35,800	39,000	22,000	18,500	21,500	6	4	4.5	12.6
891		38,800	37,200	38,800	21,000	20,000	21,000	6	5	5.5	13.0
910		39,800	34,800	38,600	19,500	17,000	19,500	6.5	4	6.5	12.3
910-1		38,600	35,500	38,400	20,000	18,000	19,000	6	4	5	12.5
Average........		39,375	35,825	38,700	20,625	18,375	20,250	6.1	4.2	5.3	12.6
Published values			34,000	38,000		16,000	19,000		3	5	Superheated

[a] The metal was melted down in welded steel pots. It was refined with commercial refining flux at 740°C. When the melt had reached 760°C. it was treated with carbon and the metal was then allowed to drop back to casting temperature in a 10 to 20-min. period. Casting temperature was 710° to 720°C.

The mechanical results are based on rough-surfaced nonmachined test bars cast in high-permeability sand from 60-lb. melts. Commercial heat-treatment practices were followed throughout.

TABLE 5.—*Tensile Properties of Sand-cast Carbon-treated*[a] *A.S.T.M. No. 17 Alloy*

Heat No.	Condition	Tensile Strength, Lb. per Sq. In.			Yield Strength, Lb. per Sq. In.			Elongation, Per Cent in 2 In.			Magnesium Grain Size[10]
		Maximum	Minimum	Typical	Maximum	Minimum	Typical	Maximum	Minimum	Typical	
903	As cast	22,500	22,100	22,300	17,000	14,000	16,000	1.5	1.5	1.5	12.2
903-1		23,200	22,100	22,600	16,000	15,500	16,000	2	1	2	12.2
911		24,800	22,200	23,100	17,500	14,000	17,000	2	1	1.5	12.0
911-1		24,100	22,100	23,500	15,000	14,000	15,000	2	1	2	12.6
Average........		23,650	22,125	22,875	16,375	14,375	16,000	1.9	1.1	1.8	12.2
Published values			20,000	24,000		10,000	16,000		1	2	Superheated
903	Heat-treated (fused salt)	37,800	36,000	37,700	18,000	17,000	18,000	9.5	8.5	9	12.0
903-1		39,200	34,000	38,000	17,000	15,000	16,000	10.0	7	9	12.8
911		38,800	36,000	38,100	17,000	14,000	16,000	11.5	9	11.5	12.3
911-1		37,300	36,500	37,200	18,000	13,000	15,500	12.0	10	11	12.0
Average........		38,275	35,625	37,750	17,500	14,750	16,375	10.8	8.6	10.1	12.3
Published values			32,000	39,000		10,000	16,000		6	10.5	Superheated
903	Heat-treated aged	38,500	33,200	37,500	27,000	20,000	23,000	2	1.5	2	13.0
903-1		39,500	35,500	38,000	26,000	23,500	24,000	2	1.5	1.5	12.2
911		39,000	36,900	38,800	25,500	22,500	25,000	2	1	1	12.0
911-1		38,400	34,100	37,200	26,500	21,500	25,000	3	1	2	12.5
Average........		38,850	34,925	37,875	26,250	21,875	24,250	2.3	1.1	1.6	12.4
Published values			34,000	40,000		18,000	23,000		1	2	Superheated

[a] The metal was melted down in welded steel pots. It was refined with commercial refining flux at 740°C. When the melt had reached 760°C. it was treated with carbon and the metal was then allowed to drop back to casting temperature in a 10 to 20-min. period. Casting temperature was 710° to 720°C.

The mechanical results are based on rough-surfaced nonmachined test bars cast in high-permeability sand from 60-lb. melts. Commercial heat-treatment practices were followed throughout.

TABLE 6.—*Tensile Properties of Sand-cast Carbon-treated*[a] *A8 Alloy*

Heat No.	Condition	Tensile Strength, Lb. per Sq. In.			Yield Strength, Lb. per Sq. In.			Elongation, Per Cent in 2 In.			Magnesium Grain Size[10]
		Maximum	Minimum	Typical	Maximum	Minimum	Typical	Maximum	Minimum	Typical	
889	As cast	23,800	22,800	23,500	13,000	11,500	12,500	4	3.5	4	11.5
889-1		25,600	24,000	25,400	14,500	11,000	13,500	5.5	3.5	4	12.0
913		24,000	23,500	23,700	13,000	11,500	13,000	4.5	3	3.5	11.8
913-1		23,600	22,700	23,400	15,000	10,000	12,500	4.5	4	4	11.8
Average........		24,250	23,250	24,000	13,875	11,000	12,875	4.6	3.5	3.9	11.8
"Superheat" values........				23,000			10,000			4	Superheated
889	Heat-treated (fused salt)	35,100	34,000	34,600	14,000	13,000	13,500	12	10	11.5	11.3
869		37,800	36,200	37,200	14,000	13,000	13,500	15	13	14	12.0
913		37,100	35,100	36,300	14,000	12,500	13,500	15	10	12	11.6
913-1		37,900	34,800	37,200	13,500	12,500	13,000	13.5	11	13	10.9
Average........		36,975	35,025	36,300	14,125	12,750	13,375	13.6	11	12.6	11.5
"Superheat" values........				37,500			14,000			15	Superheated
889	Heat-treated aged	35,700	33,200	35,400	16,500	14,500	16,000	6	5	6	11.5
889-1		38,100	37,400	38,100	20,000	19,000	19,500	7	6	6.5	12.0
913		33,900	31,600	32,800	19,000	14,500	18,000	4	3.5	4	11.7
913-1		38,000	33,000	37,000	19,500	15,500	18,000	7	4.5	5.5	11.5
Average........		36,425	33,800	35,825	18,750	15,875	17,875	6	4.8	5.5	11.7
"Superheat" values........				37,000			18,000			6	Superheated

[a] The metal was melted down in welded steel pots. It was refined with commercial refining flux at 740°C. When the melt had reached 760°C. it was treated with carbon and the metal was then allowed to drop back to casting temperature in a 10 to 20-min. period. Casting temperature was 710° to 720°C.

The mechanical results are based on rough-surfaced nonmachined test bars cast in high-permeability sand from 60-lb. melts. Commercial heat-treatment practices were followed throughout.

TABLE 7.—*Tensile Properties of Sand-cast Carbon-treated*[a] *AZ91 Alloy*

Heat No.	Condition	Tensile Strength, Lb. per Sq. In.			Yield Strength, Lb. per Sq. In.			Elongation, Per Cent in 2 In.			Magnesium Grain Size[10]
		Maximum	Minimum	Typical	Maximum	Minimum	Typical	Maximum	Minimum	Typical	
906	As cast	24,600	20,700	23,300	18,000	16,000	17,000	2.5	1.5	2	12.1
906-1		23,000	22,000	22,600	17,000	14,500	15,500	2	1.5	1.5	13.0
912		21,800	20,800	21,500	17,000	13,000	16,000	1.5	1	1.5	12.3
912-1		25,600	21,100	22,700	17,500	17,000	14,000	2	1	1.5	12.3
Average........		23,750	21,150	22,775	17,375	15,125	15,625	2.0	1.3	1.6	12.4
"Superheat" values........				21,000			12,000			2	Superheated
906	Heat-treated (fused salt)	35,300	34,900	35,000	17,000	14,500	17,000	9	9	9	11.6
906-1		35,900	34,500	35,000	16,500	12,000	14,000	9	8	9	11.8
912		37,800	36,900	37,800	15,500	14,000	15,500	9	7	9	12.1
912-1		40,000	37,000	39,000	16,500	13,500	14,000	11.5	11.5	11.5	11.8
Average........		37,250	35,750	36,700	16,750	13,500	14,375	9.6	9	9.6	11.8
"Superheat" values........				34,000			13,000			8	Superheated
906	Heat-treated aged	36,500	34,000	36,300	26,000	20,000	24,000	1.5	1	1.5	12.0
906-1		35,200	35,200	35,200	25,000	19,600	24,400	2	2	2	11.8
912-1		35,400	34,000	35,000	23,400	18,600	23,400	2	1	1.5	12.6
Average........		35,700	34,400	35,500	24,800	19,400	23,600	1.8	1.3	1.7	12.1
"Superheat" values........				36,000			20,000			2	Superheated

[a] The metal was melted down in welded steel pots. It was refined with commercial refining flux at 740°C. When the melt had reached 760°C. it was treated with carbon and the metal was then allowed to drop back to casting temperature in a 10 to 20-min. period. Casting temperature was 710° to 720°C.

The mechanical results are based on rough-surfaced nonmachined test bars cast in high-permeability sand from 60-lb. melts. Commercial heat-treatment practices were followed throughout.

TABLE 8.—*Effect of Stirring on Grain Size*[10] *of A5 Alloy*[a]

Sampling and Stirring Temperature, Deg. C[b]	Melt Grain Size		Reheat Grain Size		Remelt Grain Size	
	Before Stirring	After Stirring	Before Stirring	After Stirring	Before Stirring	After Stirring
650	11	11	12	12	13	13
700	11	11	12	12	12	12
725	11	11	12	12	12	12
750	9	9	12	12	9	9
775	8	9	12	13	8	13
800	9	9	12	13	8	13
825	9	10	12	13	12	12
850	10	12	13	13	13	13
900	13	13	14	14	13	13

[a] Data taken on 30-lb. melts.

[b] At each temperature indicated the melt was sampled and then stirred vigorously for three minutes before being sampled again.

DISCUSSION OF RESULTS

The mean curves of Fig. 1 show that when an alloy of the Elektron A5 type (5 per cent Al, 0.3 per cent Zn) that has not been treated with carbon is melted the test castings can be expected to have a magnesium grain size of approximately 11 to 10 (0.007 to 0.010 in. intercept value) when cast at 650°C. As the casting temperatures approach 800°C. (1472°F.) the expected grain sizes increase to a maximum of the order of 8 to 7 (0.02 to 0.028 in. intercept value). When ingots are cast at higher temperatures—i.e., in the superheated range between 800° and 900°C. (1472° to 1652°F.), increasing refinement is noted, and at 900°C. a grain size of about 12 (0.0058 in.) may be expected. As the melt is cooled after superheating and castings made at successively lower temperatures down to 650°C., coarser grain sizes are noted, and finally, at 650°C., a grain size approximately that found at the same temperature on the heating cycle is obtained.

When nonsuperheated melts are cooled from 800°C. the test pieces cast at various temperatures have approximately the grain size obtained at the same temperatures on the corresponding heating cycles. It is apparent that castings from nonsuperheated melts have grain sizes that are proportional to the casting temperature on both the heating and the cooling cycles and the two curve sections representing these cycles are mirror images of each other. A study of carbon-treated melts reveals that the test castings at 650°C. have a grain size of 13 (0.0035 in.), which is considerably finer than that obtained with normal melts that have not been carbon treated. Some initial coarsening is noted with increasing temperature up to approximately 725°C. (1337°F.), but an additional grain-refining effect is evident when the casting temperatures exceed this point. When the casting temperature of only 800°C. (1472°F.) has been reached the obtained grain size is 14 (0.0025 in.), which is fully two sizes finer than was obtained by casting from superheated melts at the temperature at which maximum refinement resulted, 900°C. (1652°F.). Some coarsening is evident on the cooling cycle and this part of the curve roughly parallels the cooling cycle of the superheated melts. The final grain size at 650°C., however, is 13 (0.0035 in.), or more than two sizes finer than that obtained from the superheated melts at the same temperature. The graph evidences that carbon-treated melts will produce castings of 13 to 13½ grain size for any casting temperature above 700°C. (1292°F.), and that this grain refinement and its control is obtained by carbon treatment without resort to superheating. The grain-refinement effect of the carbon treatment for this Elektron A5 type alloy is much greater than that obtained with the usual high-temperature superheating practice.

Similar consideration of Fig. 2 for the Elektron A8 type alloy (8 per cent Al, 0.4 per cent Zn) shows that there is a tendency for this alloy to produce castings of a finer grain size, at corresponding temperatures, than is found with the Elektron A5 type alloy. The higher aluminum content of the A8 alloy is responsible undoubtedly for this effect. It is also noted that the grain-refining effect of the carbon treatment takes effect immediately at 650°C. and increases as a casting temperature of 800°C. is approached. Castings taken on the cooling cycle show some coarsening when cast from either superheated or carbon-treated melts, but carbon-treated melts produce castings of about one grain-size number finer at corresponding temperatures.

Fig. 3, for A.S.T.M.-17 alloy (9 per cent Al, 2 per cent Zn) shows that the grain-refining effect of superheating is still more pronounced than with alloys of a lower total content of aluminum and zinc. The carbon-treated melts produce about the same grain sizes as are obtained by casting from superheated melts at corresponding temperatures. Nonsuperheated melts produce castings of about the same characteristics as previously described for A5 and A8 type alloys.

Fig. 4, for the A.S.T.M.-4 alloy (6 per cent Al, 3 per cent Zn) shows that while nonsuperheated melts behave about the same as previously described for Elektron A5, Elektron A8 and A.S.T.M.-17 alloys, the grain-refining effect of both superheating and carbon treatment on this alloy is still greater than is their effect on the other three alloys. The relatively high zinc content apparently more than makes up for the lower aluminum content of this alloy. It is remarkable that the castings taken from the carbon-treated melts at any temperature above 650°C. have grain sizes finer than 14 (0.0023 in.).

Fig. 5 shows that A.S.T.M.-2 alloy (10 per cent Al) behaves similarly to A.S.T.M.-17 alloy except that the maximum refinement of the grain size is about one size smaller, or 15 (0.0018 in.), than with A.S.T.M.-17. This chart can also be considered as typical of the results obtained with the Elektron AZ91 alloy (Al 10.0 per cent, Zn 0.5, Mn 0.3), as is shown by the data of Table 7.

Fig. 6 summarizes the results of more than two thousand casts from 110 individual heats. It emphasizes the poignant fact that the grain-refining effect of carbon on nonsuperheated melts of the commercial aluminum-containing alloys treated is more pronounced than is the effect accomplished by superheating and is less subject to the variations that are normal to the usual superheating practice. It evidences that when melts of these alloys are heated from 650° to 800°C., the grain phenomena for the nonsuperheated and the carbon-treated melts are divergent in effect over the range of 650° to 800°C. It also shows that there is a narrower spread of grain-size values on the cooling cycle for these alloys in the carbon-treated condition than for the superheated condition. Consequently, the grain size of castings produced from the carbon-treated melts is less dependent upon alloy content and casting temperature than when produced from superheated melts.

The spread of grain-size expectances for the aluminum-bearing group of alloys apparently follows a fixed and well defined pattern, dependent on the manner in which the metal has been treated and the thermal aspects of the melt. The remarkable degree of grain-size control achieved by carbon inoculation is clearly defined in this chart.

Fig. 7 presents no additional results, but if the meaning of the separate charts already discussed, from which it is composed, is understood, this summary chart, showing an assembly of the mean results for each of the alloys studied, may be used to advantage for final consideration of the factors that influence the grain refinement of the industrial magnesium alloys.

The graphs of grain size versus casting temperature over heating and cooling ranges from 650°C. up to 900°C. and back to 650°C. for the alloys are in the shape of distorted sine curves, and may be called grain-cycle curves, for convenience.

The three segments of these grain-cycle curves suggest a three-stage mechanism. The first segment, to the crest of the sine and represented by the thermal increase from 650°C. to approximately 800°C., would appear to be a region in which coagulation of nuclei-forming constituents is taking place. Apparently the maximum coagulation is realized somewhere in the temperature region of 800° to 825°C. The second stage is represented by the segment of the curve that lies between the rising temperatures of 800° and 900°C. In this region it would appear that the previously coagulated nuclei-forming constituents are becoming increasingly able to break down into multiple units or cloudlike nuclei when exposed to a sudden change of thermal or mechanical conditions. The maximum grain-refining achievement in this direction is centered apparently at 900°C. The third stage is represented by the segment of the curve that identifies the cooling cycle of the melt and on the chart covers the temperature region of 900° to 650°C., falling temperature. In this stage it seems evident that some coagulation of the grain-forming nuclei is taking place, which is restricted and in no wise approaches the degree of coagulation observed in the first stage, which apparently occurs only on remelting after freezing has occurred.

The phenomena of the second stage in this cycle might be explained by the conceptions of other investigators. If some elements and compounds were capable of dissolving at elevated temperatures and their solubilities were effected by sudden changes, such as temperature, their precipitation as cloudlike nuclei during casting would produce numerous centers of crystallization and a resulting fine grain size. The precipitation of iron-aluminum compounds has been suggested, for instance, and, in view of these thoughts advanced by other investigators, several typical heats of the alloys were examined to determine the variation of iron content with casting temperature during the cycle of treatment. The results given in Table 9 indicate that maximum solubility of iron probably is not reached within the time and temperature periods covered by the tests described herein. Therefore, because complete grain refinement was achieved in the temperature-time cycles used, it was concluded that there is no close relationship between iron content and grain size.

TABLE 9.—*Iron Content of Cast Ingots*

Casting Temperature		Iron in Ingots, Per Cent					
		A5		A8		A.S.T.M.-4	
Deg. C.	Deg. F.	Heating	Cooling	Heating	Cooling	Heating	Cooling
650	1202	0.008	0.009	0.002	0.004	0.003	0.001
700	1292	0.009	0.011	0.002	0.004	0.001	0.001
750	1382	0.010	0.011	0.003	0.004	0.002	0.001
800	1472	0.010		0.003		0.001	
SUPERHEATED MELTS							
650	1202			0.002	0.008		0.009
700	1292			0.002	0.008	0.002	0.010
750	1382			0.002	0.008	0.003	0.009
800	1472			0.002	0.009	0.003	0.009
850	1562			0.004	0.007	0.004	0.008
900	1652			0.006		0.005	
CARBON-TREATED MELTS							
650	1202	0.007	0.010	0.003	0.003	0.003	0.003
700	1292	0.008	0.010	0.003	0.003	0.003	0.002
750	1382	0.009	0.010	0.003	0.003	0.002	0.003
800	1472	0.009		0.003		0.003	

The assembly of graphs for the carbon-treated melts indicates that the refining effect of carbon is greater above 750°C. (1382°F.) than it is at lower temperatures. This could be attributed to the greater solubility of nuclei material at higher temperatures or to some endothermic reaction responsible for the formation of nuclei-forming crystals. The authors' investigation has shown that carbon does not effect the grain size of castings from either standard magnesium or A.S.T.M.-11 (1.5 per cent Mn) alloy and indications are that aluminum must be present in magnesium alloys to obtain appreciable grain refinement by use of carbon, as is true in normal superheating practice.

Attempts were made to determine the carbon content of grain-refined ingots that had been carbon-treated. The carbon content was too low for accurate chemical analysis but combustion methods indicated that the carbon content of the metal so refined was of the order of 0.003 per cent. The War Metallurgy Committee in a later project experimented on this method of grain refinement and reported, "This indicated the formation of Al_4C_3 as the effective grain-refining constituent . . . Al_4C_3 appears to produce good grain refinement if it is not used in excess; i.e., about 0.01 per cent by weight."* This figure of 0.01 per cent Al_4C_3 added by weight is chemically equivalent to 0.0025 per cent C and closely checks the indicated value of 0.003 per cent C found in the carbon-treated alloys of this investigation. The Al_4C_3 theory, which seemingly is advanced in the report quoted above, is very attractive, but offers some complications that make it difficult to accept at this moment. The report indicates that there is a definite limit to the amount of Al_4C_3 that can be used to obtain grain refinement and that an excess over that limit may cause loss of the effect. It would seem likely that, in the latter instance, the excess Al_4C_3 was serving as large nuclei, which produced coarse grain and offset the beneficial effect of much smaller nuclei available from the presence of a minute quantity of the Al_4C_3. The thermodynamic data for Al_4C_3, as presented by K. K. Kelly,[11] indicate that Al_4C_3 is a stable compound over the full range of temperature in which carbon was introduced into magnesium alloy melts in this investigation. The authors are not familiar with any data that may exist concerning the stability of dilute solutions of Al_4C_3 in magnesium, however, despite the fact that they have added excessive amounts of carbon in a number of tests, they have been unable to detect the presence of any Al_4C_3 in any of the test castings produced. If Al_4C_3 can be considered as the constituent responsible for grain-refining action, it would seem obvious that some evidence of its presence could be detected when excess carbon has been made available for its formation. It would appear more logical that some compound of magnesium with Al_4C_3, or of aluminum, magnesium and carbon, which is unstable at low temperatures, is being formed. Such a compound might release carbon in a submicroscopic form on change of the physical state of the melt to serve as nuclei for fine grain formation.

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* Defense Plant Corporation and Army approval granted for these references.

Other investigators have indicated that grain refinement may be induced by vigorous stirring of the molten alloy.[6b] Table 8, showing a few of the authors' results on stirring, outlines the degree of grain refinement obtained on the A5 alloy by this method. Their stirring experiments were made early in the investigations of grain size, in order to determine whether the phenomenon of grain refinement was primarily a function of the stirring action or was due to the presence of carbon that was being stirred into the melt. Some grain-refining effect appeared evident from the simple stirring tests, as is shown by the data, but in no manner approached the degree achieved from the carbon inoculation, nor was it characterized by the permanence on holding that was typical of the carbon effect. Some later stirring efforts actually resulted in a coarsening effect which was attributed to a coagulation of the nuclei caused by the stirring action. It is of interest to note that the investigators referred to used magnesium metal from a carbothermic source in most of their experiments. The tests described herein with metal from a like source found it to be highly impregnated with carbon and it readily produced a fine-grained alloy without resort to superheating. The reported work of these other investigators was on A.S.T.M.-17 alloy from various sources, including electrolytic processes. Their results may have been influenced by the very small heats utilized in the study. For the tests described in this paper an extensive study was made of stirring effects on 150-lb. heats of metal during the last phase of the investigation. This study was made on several different alloy compositions and was instigated because of grain-refining effects that had been noticed on some small heats of metal that had been stirred. Grain refinement occurred in less than 40 per cent of these 150-lb. heats and could not be duplicated with regularity in spite of precautions of increased stirring time and effort.

The authors feel that a theory of carbon inoculation offers an opportunity for logical explanation of the unusual phenomena frequently encountered in grain-refining efforts with the industrial magnesium alloys of the aluminum-bearing group. The extremely small quantity of carbon required for the effect makes it easy to accept an expectation of a wide variation of achievement. Such circumstances as dust-laden atmospheres, products of combustion, dirty tools and utensils, might well be effective on temperature requirements and resultant grain-refining achievements. A much higher temperature need could be expected when minimum quantities of carbon were available than when an excess of carbon was supplied. The high temperature requirement of normal superheating practice would seem to be a logical expectation in view of the minute quantity of carbon available in the usual melt, particularly when it is found that with excess carbon made available the temperature requirement for grain refinement is reduced to a range not exceeding 750° to 800°C.

The authors' investigation has shown that a remelt of a previously superheated melt will achieve maximum grain refinement at a temperature approximately 50°C. lower than was necessary on the first superheating effort. This suggests the probability that an additional small quantity of carbon is picked up in the pigging off and remelting operation, with a resultant increase of total available carbon. It would also appear that a coagulation or gathering together of the previously dispersed nuclei tends to occur during the remelt of a superheated or grain-refined melt, resulting in a loss of refinement and the need for a return to some elevated temperature to effect redispersion. The typical upward trend on the cooling cycle of all the grain-refined curves indicates that some such loss of nuclei must occur.

PRACTICAL ASPECTS

Good superheating practice has long been considered very important in the production of high-quality magnesium-alloy castings and the primary controlling factor for securing a satisfactory fine grain. It has been generally acknowledged that grain refining improves ultimate tensile strength, tensile yield strength, impact strength, and elongation. Results of recent investigations have reconfirmed these beliefs and also the fact that fineness of grain decreases the time required for satisfactory solution heat-treatment. However, superheating is one of the most annoying requirements that have been imposed on magnesium foundry operations. The additional time and temperature requirements are an important economic factor and limit the production from available equipment. These economic factors add to the difficulties that magnesium foundries must overcome to meet competition.

It appears that this expensive and time-consuming step can be eliminated through low-temperature grain-size control by inoculating the melts with carbon.* This can be accomplished by a simple and economic procedure of passing a suitable gas through the melt or by stirring finely divided carbon or carbonaceous material into the melt at temperatures not exceeding those required for ordinary refining or casting operations. It may also be accomplished by the direct addition of aluminum carbide,[5a] though all the factors that may be connected with such an addition have not been worked out at this writing.

Results of the investigations described herein have shown that propane is a suitable gas and that effective solid materials are pitchcoke, graphite and lampback. The carbon requirement to give effective grain refinement is from 0.1 to 0.2 per cent of the alloy treated. Apparently no harmful effects are caused by the use of excessive quantities of carbon aside from the creation of a dirty melt. Full grain refinement, superior in consistency to that obtained from high-temperature superheating, is obtained by addition of carbon at or near the melting range of the alloy followed by heating to a temperature that need not exceed 800°C. (1472°F.) and casting at any usual casting temperature. Substantial grain refinement is obtained without heating to 800°C. (1472°F.) but heating to this temperature thins the melt and facilitates the settling of excess addition agent or other contaminants from the melt before pouring and casting.

The maximum size of melts that can be effectively refined by carbon inoculation is not yet known, although tests have been made on 2-ton heats. No satisfactory procedure has been worked out that will give consistent and reproducible results on the 4000-lb. melts, but melts up to 300 lb. of alloy have been treated with excellent results, using either carbon or gas. It is anticipated that more effective ways of introducing carbon will be developed and that this will permit treatments of very large heats. Apparently the principal problems in connection with the practical application of this method lie in effectively distributing the carbon throughout the heat and in obtaining intimate contact between the carbon particles and the molten alloy. It has been found, for instance, that the presence of liquid flux phases, such as characterize the usual melting fluxes, tend to retard the action, and if present in quantity may even prevent it. This we believe to be due to an insulating function of the liquid flux, which envelopes the carbon and prevents it from coming into actual contact with the alloy.

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* The Century Metalcraft Manufacturing Corporation of Los Angeles, Calif., has used this process on a production basis for almost a year. In May of 1944, Mr. C. J. Amick agreed to his company's trying the process and under the supervision of C. H. Adams, Chief Metallurgist, it was rapidly put into production. They have reported a very satisfying success with the process and it has relieved a production capacity strain on their floor.

The results of tests (Tables 3 to 7) on bars cast from the carbon-treated melts of the commercial alloys show that the mechanical properties of the heats refined with carbon were as satisfactory as the properties obtained from the best superheating practice. The test bars used were cast in green sand having an A.F.A. fineness number of 60 to 70 and an A.F.A. permeability number of 160, and as a result the surfaces of these bars are relatively rough. Considering the notch-sensitive nature of magnesium alloys, it is possible that equally sound bars having a smoother finish would have higher properties than are shown in these tables. This is borne out by the report of the War Metallurgy Research Project,[5a] which gives higher values on A.S.T.M.-4 alloy after carbon treatment than were obtained in the experiments described here.

No attempt has been made in this paper to record all the tests made to investigate grain-size phenomena. However, there are several additional practical aspects to the superheating problem covered by the tests which are worth noting. For example, it has been observed repeatedly, on castings made from melts that have been superheated to 900°C. in the ordinary manner and then cooled to a temperature close to freezing before being raised to the casting temperature, that most of the grain-refining effects from the superheating are lost and the castings have the same grain size as castings made just after melting without superheating. Such cooled melts must be superheated again before the finest grain size can be obtained.

Also, it has been noted repeatedly that melts that have been once superheated and then allowed to freeze must be resuperheated in order to attain full grain refinement. However, the addition of wrought and machine scrap to such remelts undoubtedly leads to some grain refinement, which may possibly be explained by the carbon-bearing materials usually present on such material.

SUMMARY OF RESULTS

Experiments have been made to determine a procedure for grain-size control of magnesium alloys, including the Elektron A5 and A8 type alloys, and the A.S.T.M. alloys 2, 4, and 17 as made from electrolytic magnesium. The characteristic grain size as related to casting temperature for certain conditions of experimentation were investigated and the effect of carbon inoculation was determined.

Results show that grain-size control can be obtained by carbon inoculation at considerably lower temperatures than is required for ordinary superheating practice. The results of tests lead to the following conclusions:

1. Test castings from melts of nonsuperheated metal of the alloys investigated have grain sizes that indicate a regularly increasing coarseness with increase in temperature from 650° to 800°C..

2. Test castings from melts of these alloys over the range of temperatures between 800° and 900°C. show progressively increasing grain-refinement effects typical of superheating.

3. Test castings from superheated melts at temperatures between 900° and 650°C. on the cooling cycle indicate a gradual but limited loss of grain refinement.

4. Grain-refinement effect, as measured by grain size of test pieces cast at 900°C., increased with increasing aluminum content, or total aluminum and zinc content; the least effect was obtained with Elektron A5 type alloys and the maximum effect with A.S.T.M.-2 alloy. (This general relationship holds over the range of temperatures from 900°C. down to 650°C. on the cooling cycle.)

5. Test castings from carbon-treated melts, even though the melts have not been heated higher than 800°C. (1472°F.), show as fine a grain structure as do test castings from superheated melts. (In alloys containing 5 to 6 per cent Al, such as alloys Elektron A5 and A.S.T.M.-4, the carbon inoculation produces a much greater refining effect than does regular superheating.)

6. The mechanical properties of sand-cast magnesium alloys containing aluminum, treated by carbon and not superheated in the as-cast, solution-treated, and aged conditions, were as satisfactory as and more consistent than the best properties of the corresponding alloys that had been given the regular superheating treatment.

7. When melts of the alloys investigated were superheated, cooled and solidified and then remelted the grain-refining effect of superheating was substantially lost, and resuperheating or carbon inoculation was necessary for complete recovery of grain refinement.

8. When melts of the alloys investigated were superheated, cooled to just above freezing zones, but not solidified, the finest grain sizes could be obtained again only by resuperheating or by carbon inoculation.

9. The cause of grain refinement by high temperature is not known but it seems probable that cloudlike foreign nuclei formed either as a result of inoculation or by the precipitation of elements or compounds with high melting points serve as centers of crystallization for the formation of numerous grains and hence a fine-grained structure.

10. The retention of fine-grained characteristics, after remelting ingots or scrap produced from carbon-treated melts, is marked and, while reinoculation is advisable with each remelting operation, a re-treatment for establishment of grain size is not of as critical importance as it is with superheated ingot or scrap.

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DISCUSSION

R. R. Hultgren.[*]—Unfortunately each investigator of grain size seems to use a different method of designating it. It would seem that some simple, universal method could be adopted, which would apply to all metals. This ought to be in terms of grain per unit area, area per grain, or "average" diameter of grain, which has been used as the square root of the area per grain. The A.S.T.M. austenitic grain-size numbers are an artificial invention, whose only merit is that it permits the grain size of a steel to be expressed as a small integer. To invent still a new method for magnesium contributes nothing to clarify the confusion.

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Any standard accepted internationally will have to be in the metric system; hence it would be desirable to establish grain size in metric units. In this case metric units fit into practice fully as easily as do English units. It is desirable to choose them so that ordinary grain sizes are expressible in integers that are not too large. Three measuring units that fulfill this condition are given in Table 10.

TABLE 10.—*Measuring Units*

UNIT	USUAL RANGE OF GRAIN SIZES IN MAGNESIUM
Grains per square millimeter........	5 to 1000
Grain diameter in microns $= \frac{1000}{\sqrt{\text{grains/sq. mm}}}$..............	447 to 32
Grain area in 1000 sq. mm. $= \frac{1000}{\text{grains/sq. mm}}$................	200 to 1

C. H. MAHONEY (author's reply).—Dr. Hultgren's valued comments are much appreciated, particularly since he calls attention to the need for a simple universal method for grain-size designation that could be readily adopted to apply to all metals.

The method of designation we have used in this paper was outlined in a previous paper (see ref. 10), in which we included a table of the various methods for recording grain size and showing their relationship to each other. This table shows, we believe, that the A.S.T.M. method for designation of austenitic grain sizes can readily be correlated to grains per unit area or to "average" diameter of grain in either the metric or English system. Our object was not to devise some new and strange method for designating the grain sizes in magnesium alloys but to adapt such designations to past methods and, if possible, align them with previously accepted A.S.T.M. methods, which may or may not desirably be modified. We also wanted to draw attention to the merit of the austenitic system of arithmetical progression.

The authors feel that a system such as Dr. Hultgren suggests, which can be universally acceptable, must be adaptable to industrial as well as academic thinking, and that academicians should accept that a universal system, if it is to be accepted freely by both academic and industrial groups, should bow to industry's reluctance to use other than the simplest of mathematical formulas. It is our feeling that any system that is to be universally accepted must have a very direct relationship to actual measurement and should avoid logarithmic factors or even inverse factors of the actual measurement or its roots.

C. H. LORIG.*—It would have been clearer to most readers had the authors expressed grain size in inches with the grain-size numbers as an alternate or supplementary method. The former method is more widely used and expresses grain size accurately in a manner that is readily visualized. Grain-size numbers, on the other hand, have no direct physical significance.

It seems unfortunate that the authors did not base their work on grain sizes of sand castings. There is little practical value for grain-size determinations on chill-cast specimens, therefore such determinations are not of great importance. It is mainly in castings that the matter of grain size is significant. While it is possible that the grain sizes of chilled castings parallel that which would have been found in sand castings, this need not necessarily be true. Certainly coarser grains would have been found in the unchilled sand castings.

The assumption is made that Al_4C_3 must decompose before it could serve as nuclei. This is quite erroneous, as it is merely necessary that the compound precipitate out of the liquid melt at the proper temperature to form nuclei. Thus these nuclei would be Al_4C_3 if it did not decompose or carbon if it did decompose into its constituents. Furthermore, existing thermodynamic data do not indicate the stability of dilute solutions of Al_4C_3 dissolved in a magnesium melt. If Al_4C_3 is the active grain-refining constituent, the very minute amounts would make it difficult to detect as the compound.

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* Battelle Memorial Institute, Columbus, Ohio.

R. S. Busk.*—The authors' data add much to a clearer understanding of a puzzling phenomenon. The fundamental importance of carbon in the metallurgy of magnesium is becoming increasingly apparent. Contributions clarifying this relationship are of value to the technology of the magnesium industry.

There are a few points, however, I would like to mention. The quoted published values for mechanical properties reproduced in Tables 4 and 5 for A.S.T.M. No. 4 and A.S.T.M. No. 17 alloys appear low. Production averages based on tens of thousands of test bars over a period of one year are as given in Table 11. Comparison of these figures with those of Tables 4 and 5 indicates a slightly lower tensile strength for the carbon-treated melts. The published minima, of course, are not observed minima, but specification limits.

TABLE 11.—*Production Averages*[a]

Alloy		Tensile Strength[b]		Yield Strength[b]		Elongation, Per Cent	
		Minimum	Typical	Minimum	Typical	Minimum	Typical
A.S.T.M.-4	AC	24	29	10	14	4	6
	HT	34	40	10	14	7	12
	HTA	34	40	16	19	3	5
A.S.T.M.-17	AC	20	24	10	14	1	2
	HT	34	40	10	16	6	10
	HTA	34	40	18	23	1	2

[a] From the 1944 Dowmetal Data Book.
[b] In units of 1000 lb. per sq. inch.

There is excellent agreement between the tensile values reported in this paper and that previously reported by us (p. 266, this volume), with one exception. The tensile strength for A.S.T.M.-4 in the heat-treated state appears low. Could this be due to incomplete solution heat-treatment?

It is not clear how Table 9 shows anything regarding liquid solubility of Fe at elevated temperatures. There is no indication of equilibrium being established at any temperature.

A word of warning regarding excessive carbon in the melt should be added to the authors' statement on page 345. Free carbon can act as centers of corrosion in the presence of an electrolyte, and may lead to an undesirable corrosion rate in certain atmospheres. This should be recognized and guarded against.

There have been several statements in the literature recently to the effect that aluminum is necessary in magnesium alloys for a superheating effect. These statements apparently are based on a limited number of experiments with Mg-Al; Mg-Zn; Mg-Mn; Mg-Mn-Zn; Mg-Al-Mn; and Mg-Al-Mn-Zn. It is true that within these systems the presence of aluminum is very beneficial. There are, however, other magnesium-base alloys that also show a grain refinement when superheated. Among these are alloys containing Ag, Sn, or Pb with no Al.

C. H. Mahoney.—Dr. Busk's comments are greatly appreciated by the authors, who realize the extensive work he and his associates have devoted to the subject of this paper.

The published values for mechanical properties quoted in Tables 4 and 5 were taken from the handbooks of producers in the field. We realized that these values may not represent the best achievement that may be obtained with the alloys in question, nor even represent the achievement to be expected from the best and most improved practices. On the other hand, the values listed for the carbon-treated metal were arrived at by deliberately eliminating the highest values obtained from this treatment. It should be pointed out that the effect of the carbon treatment was not so much one of obtaining higher mechanical values than was possible with superheated metal but that the results were consistently on the high side of possible achievement, and therefore the typical and average values were effectively increased. Under a standardized founding practice the mechanical values obtained from the carbon-treated metal were characterized by a higher level than those we were able to obtain from superheated metal. It is quite probable that our values from the A.S.T.M.-4 alloy in the heat-treated state would have been improved by longer solution heat-treatment.

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* Dow Chemical Co., Midland, Michigan.

Table 9 was presented as indicatory evidence that in the cases studied the precipitation of iron-aluminum compounds could not be a source of the grain-size refinement, since equilibrium evidently had not been established under the temperatures of the treatment.

Dr. Busk's warning in regard to excessive carbon in the melt is quite timely, as entrapped carbon unquestionably would be a source of corrosion trouble. However, owing to the difficulty with which carbon is wetted, apparently it frees itself from the metal quite readily, and we were unable to find, either microscopically or by corrosion tests, any evidences of such entrapped carbon.

It would be very interesting to know whether carbon affected grain refinement on magnesium alloys containing silver, tin or lead in the absence of aluminum. We had no opportunity in this study to investigate such alloys and feel that a knowledge of their responses to carbon treatments would add considerably to the industry's understanding of the phenomenon that occurs at superheating.

The Solubility of Manganese in Liquid Magnesium

By N. Tiner,* Junior Member A.I.M.E.

(Cleveland Meeting, October 1944)

In an article on magnesium and its alloys, Gann and Winston[1] stated that manganese has a limited solubility in the liquid state. W. Schmidt[2] showed a diagram according to Joseph Ruhrmann indicating that the solubility of manganese in liquid magnesium falls from about 2.65 per cent at 790°C. to about 0.5 per cent at 675°C. The curve was extrapolated to show zero solubility at the melting point of pure magnesium (Fig. 1). This work suggested that at the lowest manganese contents it was not possible to detect either a eutectic or the formation of a solid solution, so that manganese was stated to be present in the structure as large individual crystals.

Two years after the presentation of these results, Gann[3] brought evidence to show that some manganese is capable of dissolving to form a solid solution, any excess of manganese present then assuming chiefly the form of small blue-gray particles scattered throughout the primary magnesium crystals, occasionally in clusters but seldom at the boundaries. He presented micrographs of cast alloys containing 0.1, 0.4 and 1.0 per cent manganese that show a small amount of coring around the individual particles due to solid solution, and indicate that the location of the manganese particles is closely associated with the original dendritic structure of the primary crystallization. He also pointed out that the amount of manganese that can be dissolved in magnesium depends on the amount of other alloying elements present, the effect of the second alloying element being to decrease the amount of manganese retained in the alloy.

E. Schmid and G. Siebel[4] have determined the solid solubility of manganese and its variation with temperature by means of precision X-ray diffraction measurements. They found that the solubility is 3.4 per cent at 645°C. and decreases to practically zero at 200°C.

It is apparent that the X-ray diffraction measurements of Schmid and Siebel are not in agreement with the results of Ruhrmann as presented by Schmidt. This disagreement, and also the lack of data on magnesium-aluminum-manganese and magnesium-zinc-manganese systems, led the author to the present investigation, to determine accurately the liquid solubility of manganese and its variation with temperature.

Experimental Method

The experimental method for making solubility determinations consists of saturating the molten magnesium or the alloys with manganese at various temperatures and analyzing the dip samples taken from these melts.

Melting is carried out in a cylindrical steel pot heated by an electric resistance furnace. The pot had a metallic outside coating to protect the steel against oxidation, and a graphite inside lining to prevent the contamination of the melt by prolonged contact with iron. The inside diameter of the pot was 4 in. and the depth 12 inches.

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* Permanente Laboratory, Stanford University, Palo Alto, California.

[1] References are at the end of the paper.

A common magnesium flux (Permanente No. 7 flux) is melted in the pot and when it is hot pure magnesium is added (1700 to 1800 grams) with a sprinkling of powdered flux to inhibit burning. The magnesium used was a special ingot magnesium analyzing approximately: iron, 0.001 per cent; lead, 0.01; silicon, 0.005; calcium, 0.005; copper, 0.001; aluminum, 0.000; nickel, 0.000.

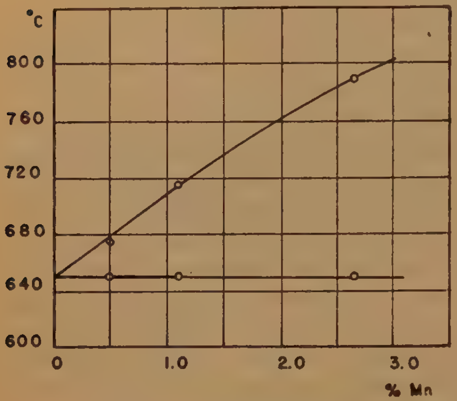

FIG. 1.—MANGANESE-MAGNESIUM DIAGRAM ACCORDING TO RUHRMANN AS REPORTED BY W. SCHMIDT.

When the charge is thoroughly molten, the slightly preheated pieces of electrolytic manganese are added and the melt is carefully stirred with a graphite rod. The impurities are raked off, and more flux is added until the melt acquires a bright surface. When refining is completed the surface of the melt is covered with a thin layer of flux. The temperature, which is measured with a Chromel-Alumel thermocouple protected by an iron sheath, is brought to a desired point and kept constant within about 5°C. by hand regulation of current input.

The metallic manganese partly dissolves in molten magnesium, and the excess sinks to the bottom of the pot. Samples, weighing from 40 to 50 grams, are taken at intervals of an hour from near the surface of the metal, with a small steel scoop, and immediately poured into graphite molds. The resultant solid is drilled in the normal way and the drillings are analyzed for manganese by bismuthate method. The drillings are thoroughly mixed and the analysis is carried out in duplicate to minimize the error that may result from the segregation of manganese. After each sampling the melt is stirred for about 5 min. and then allowed to stand until the next sampling.

A solvent can generally be saturated in two ways: (1) an excess of solute is agitated with the solvent, at a definite temperature, until equilibrium is attained, or (2) the solvent is heated with an excess of the solute to a temperature higher than that at which saturation is required, and then cooled to the desired temperature. The two procedures should give practically the same result, provided sufficient time is allowed for the establishment of equilibrium, and provided the solid solute is always present in excess. This point has been considered in the present investigation, and to check the results, the limit of saturation, in certain cases, is determined by two different procedures.

It should be noted here that the molten metal has a strong tendency to react with the atmosphere at high temperatures and to solidify on the sampling scoop at low temperatures near the freezing point. These difficulties are partially overcome by adding new flux and some sulphur on the metal surface just before sampling at high temperatures, and heating the sampling scoop to 600° to 700°C. before dipping it into the melt at low temperatures. The highest and the lowest temperatures investigated were 850° and 670°C., respectively.

The amount of iron that may be introduced into the melt by the thermocouple sheath, melting flux and manganese additions is negligible. Chemical analysis showed that the samples taken from the melt, as described above, contained approximately 0.002 to 0.004 per cent iron.

DISCUSSION OF RESULTS

The results concerning the solubility of manganese in pure magnesium are presented graphically in Fig. 2, which shows that: (1) the amount of manganese dissolved in molten magnesium, at a definite temperature, increases with time and approaches a constant (limiting) value, and (2) the limit of saturation at 670°, 700°, 765°, and 850°, is approximately 2.3, 2.6, 3.9, and 6.6 per cent, respectively. The continuous curves in Fig. 2 indicate the variation of the manganese content of unsaturated melts and the dotted curves that of supersaturated melts, obtained by keeping the melt for long hours at high temperatures in contact with solid manganese and then cooling to the desired temperature.

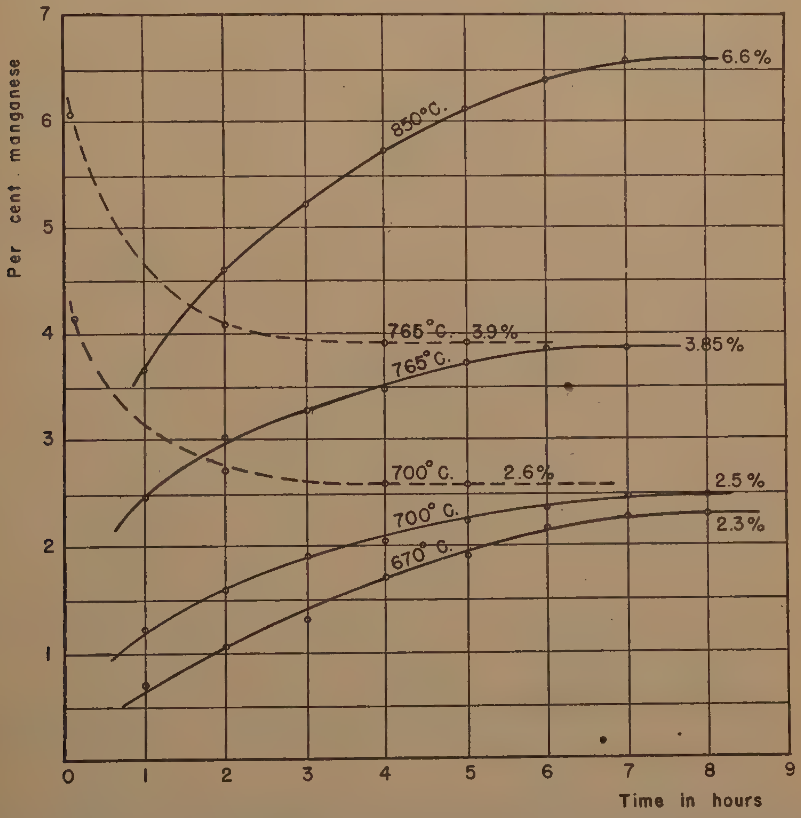

FIG. 2.—SOLUBILITY OF MANGANESE IN MOLTEN MAGNESIUM AT DIFFERENT TEMPERATURES. Continuous curves refer to unsaturated solutions and dotted curves to supersaturated solutions

The effect of the presence of other alloying elements upon the solubility of manganese in molten magnesium is also examined by adding known quantities of aluminum or zinc into the melt and determining the solubility of manganese as described above. The determinations show that: (1) magnesium melts containing 7.5 to 8.0 per cent aluminum can dissolve 1.4 per cent manganese at 800° and 0.3 per cent at 700°C., and (2) magnesium melts containing 6 per cent zinc can dissolve 3.0 per cent manganese at 800° and 1.7 per cent at 720°C.

Based on Raoult's law and Clausius-Clapeyron equation, it can be shown[5] that the solubility of solids in a liquid as a function of temperature may be expressed approximately by the equation

$$\ln N = -\frac{L_f}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad [1]$$

where N is the mol fraction of the solid in solution, L_f the heat of fusion of pure solid, R the gas constant, T the absolute temperature, and T_m the melting point of the pure solid. For manganese, substituting 1.99 cal. per degree for R, 1517°K. for T_m and 3560 cal. per mol (or atom) for L_f, one may write

$$2.30 \log N = -\frac{3560}{1.99}\left(\frac{1}{T} - \frac{1}{1517}\right)$$

or

$$\log N = 0.5127 - 777.8/T \qquad [2]$$

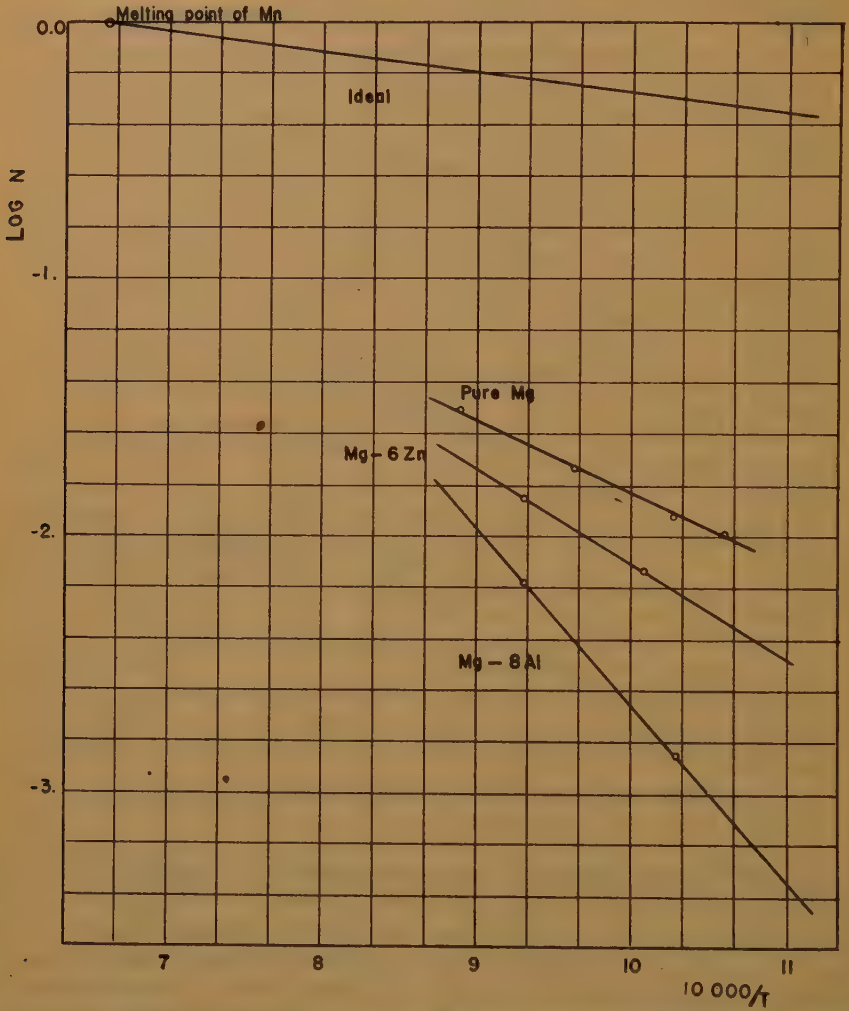

FIG. 3.—LOG OF THE SOLUBILITY OF MANGANESE IN MAGNESIUM AND ITS ALLOYS AS A FUNCTION OF THE RECIPROCAL OF ABSOLUTE TEMPERATURE.

The log of the solubility of manganese in pure magnesium (expressed in atomic per cent) as a function of the reciprocal of the absolute temperature is shown in Fig. 3. It is to be noted that the experimental points are approximately in a straight line. The data for magnesium melts containing 7.5 to 8.0 per cent aluminum or 6 per cent zinc are limited, and the straight lines drawn through two experimental points give only rough representations of the log of the solubility vs. the reciprocal temperature.

The fact that manganese is soluble at a given temperature in considerably smaller quantities in molten magnesium than in an ideal liquid, calculated by Eq. 2, and that it becomes less and less soluble as zinc or aluminum is added to the melt, may be explained by the concept of "internal pressure," that is, cohesive forces existing in the melt.

In a liquid metal composed of the solute atoms A and the solvent atoms B, one must consider the forces existing between the like atoms, A and A, and B and B, and also the forces between the unlike atoms A and B. If the forces between A and B are identical with the others, so that the average force upon any one atom is independent of the composition of the solution, the solution may be considered ideal. If the forces between A and A are greater than the others, the atoms of this species will tend to associate with themselves, squeezing out B and producing deviations from ideal condition, almost proportional to the difference of the cohesions between the like atoms. A solute of

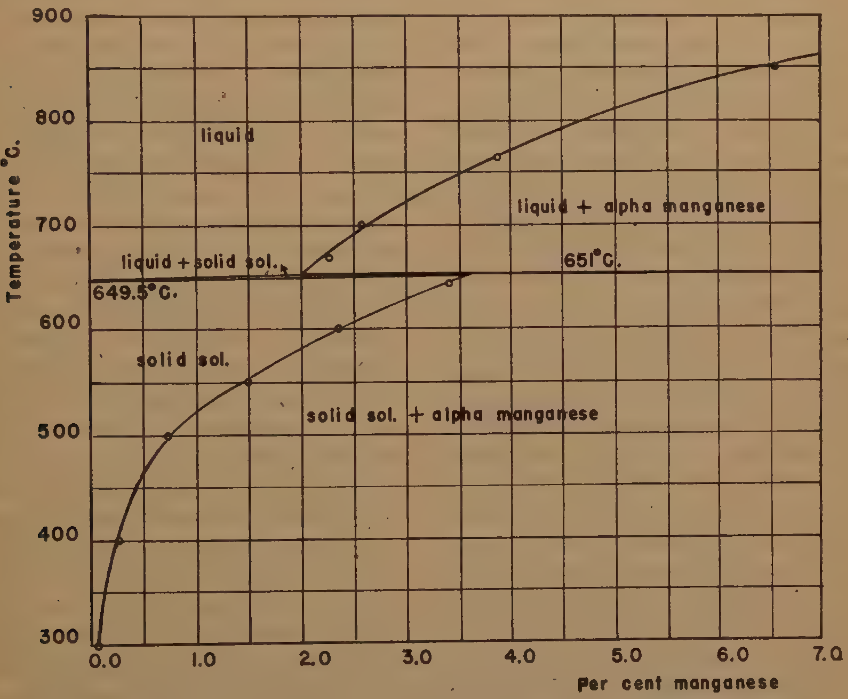

FIG. 4.—PHASE DIAGRAM OF MAGNESIUM-RICH MAGNESIUM-MANGANESE ALLOYS.
Solid solubility curve is due to Schmid and Siebel,[4] and peritectic temperature to Grogan and Haughton.[6]

high internal pressure should then show decreasing solubilities in a series of solvents of progressively decreasing internal pressure.

According to a table presented by Hildebrand,[5] the internal pressure of manganese is considerably higher than that of magnesium. It is natural, therefore, to expect the solubility of manganese to be less in pure magnesium than in an ideal liquid. The fact that the solubility in pure magnesium, at a given temperature, is further decreased by zinc or aluminum additions may be explained by assuming that the internal pressure of pure magnesium, magnesium-zinc and magnesium-aluminum alloys are progressively decreasing.

Recently, Grogan and Haughton[6] investigated the constitution of magnesium-rich alloys of magnesium and manganese. They place the solubility of manganese at somewhat higher values; particularly at the 700° to 800°C. temperature range, the discrepancy between their figures and the present data approaches 0.5 to 0.6 per cent manganese, which is larger than the inaccuracies in the present work. For the chemical analyses of duplicate samples were not different by more than 0.05 per cent manganese, and from the slope of the curve for solubility vs. the reciprocal temperature it follows that an error of about 5°C. in the temperature control leads to an error of less than 0.12 per cent manganese.

Grogan and Haughton prepared supersaturated liquid magnesium by reducing the molten metal with anhydrous manganese chloride at about 900°C. The temperature of the melt is lowered in stages, and after it has been held steady to 1°C. for about 10 min. at the desired point, a dip sample is taken from near the surface of the metal. The curves for percentage of manganese vs. time for supersaturated melts in Fig. 2 clearly indicate that such a short holding period can easily lead to incomplete settling of manganese for the establishment of equilibrium and to high manganese analyses.

The extrapolation of the log of the solubility vs. the reciprocal temperature curve (Fig. 3) shows that the solubility of manganese in liquid magnesium is approximately 2.0 per cent near the freezing point of pure magnesium (650°C.). This indicates either that the X-ray measurements of Schmid and Siebel are too high and the solid solubility of manganese in magnesium at 645°C. is less than 2.0 per cent, or that the solubility of manganese in magnesium is decreased from about 3.4 to 2.0 per cent during the melting process because of a peritectic reaction.

Based on microscopic examinations, Grogan and Haughton[6] state that the results of X-ray measurements of Schmid and Siebel are too high. However, they have not actually determined the solid solubility at various temperatures. Their thermal analysis shows a small increase in the liquidus temperature as the manganese content is increased from 0.0 to 2.1 per cent, indicating the existence of a peritectic reaction at about 651°C.

The phase diagram (Fig. 4) is constructed from the data reported in the present work and that of Schmid and Siebel.[4] The peritectic temperature is due to Grogan and Haughton. The second phase that separates from the liquid as primary crystals is reported by Grogan and Haughton[6] to be alpha manganese. The second phase occurring in the solid state beyond the solubility limit is identified by Bakhmetev and Golovchiner,[7] on the basis of Laue diffraction patterns, as beta manganese, while J. B. Hess, of the Dow Chemical Company Laboratory, states that electron diffraction analyses show the second phase to have alpha-manganese structure; presumably a solid solution of magnesium in manganese, since it was also possible to prepare alpha manganese containing up to 25 per cent magnesium at room temperature.

CONCLUSIONS AND SUMMARY

1. The solubility of manganese in liquid magnesium is limited and depends on temperature, and the log of the solubility, expressed in atomic per cent, varies approximately linearly with the reciprocal of the absolute temperature.

2. The results, concerning the solubility of manganese in liquid magnesium, are not in agreement with those of Ruhrmann as reported by Schmidt, and are slightly lower than those found by Grogan and Haughton, particularly throughout the 700° to 800°C. temperature range (the discrepancy being less than 0.6 per cent manganese).

3. Alloy additions, such as zinc or aluminum, decrease the solubility of manganese in magnesium. This effect, which depends on the amount and the nature of the alloying element added, may be attributed to a decrease in the internal pressure of the solvent melt.

ACKNOWLEDGMENT

The author is indebted to the Permanente Metals Corporation for supplying laboratory facilities, and to Dr. W. O. Wetmore and other members of the Permanente Metals Laboratory for assistance in this investigation.

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DISCUSSION

(*L. W. Kempf presiding*)

G. EDMUNDS.*—The decrease in the solubility of Mn in Mg by Zn or Al additions has been attributed by the author to the progressive decrease of internal pressure of pure Mg, Mg-Zn and Mg-Al alloys. A large change, and particularly a large reduction in internal pressure due to alloyage of Zn with Mg would appear to be anomalous, since the internal pressures of Zn and Mg differ so little. Also, since the internal pressures of Al and Zn are above that of Mg, would not an increase in internal pressure due to alloyage be expected?

The question of particulate solute metal, in suspension in the melt, being included in the sample and thus leading to erroneous, high values is at least partially answerable by sampling at two levels in the melt† or by sampling after normal and excessively long periods. If the melt is in contact with coarse particles of the precipitating phase, the greater solubility of any fine particles would cause them to disappear and additional crystallization on the coarse ones would occur. Constancy of composition of the liquid samples would indicate the completion of this process. The approach of equilibrium from undersaturation, a method used by Mr. Tiner, is, of course, excellent insurance against the suspension of fine particles.

L. W. BALL.‡—I wonder if there is anyone here who has investigated the distinction between solution and suspension, and whether this factor enters into the present analysis. The reason I ask is that when we use the X-ray micrograph technique on any commercial magnesium, we always see fine particles, having high X-ray absorption, distributed at random throughout the metal. The big difference in X-ray absorption between manganese and magnesium makes the X-ray micrograph method very suited to this problem.

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* New Jersey Zinc Co., Palmerton, Pennsylvania.

† G. Edmunds: Liquidus Determinations in Zinc-rich alloys (Zn-Fe; Zn-Cu; Zn-Mn). *Trans.* A.I.M.E. (1944) **156**, 268.

‡ Triplett and Barton, Burbank, California.

L. W. Kempf.*—Mr. Tiner does not indicate that he makes any attempt to distinguish between particles that might be suspended and a true solution. That, of course, is not at all easy to do.

Anyone who has worked with this method, adding data to constitutional diagrams, is distinctly aware of the many difficulties that are apt to arise. We did something along this line, using this method to a considerable extent on some constitutional diagrams of aluminum-base alloys. For example, one of the difficulties that always arises is that there is a tendency, at least in aluminum, for the very top surface to contain a high concentration of the element for which the constitutional relationships are being determined. There are a lot of pitfalls, but Mr. Tiner seems to have been aware of at least most of them in his demonstration; he comes to the same point both going up in temperature and coming down in temperature, which is fairly impressive.

F. N. Rhines.†—It would help in the appraisal of this work if we had a series of photomicrographs showing the structures of the alloys involved and of unsaturated alloys as well. I am personally puzzled by the possibility that was mentioned a minute ago with regard to whether or not there may still be suspended particles that did not behave as they ought to behave in settling out. It is my impression that we usually see in alloys containing less than 2 per cent of manganese what appear to be primary particles of manganese. If these are in fact primary particles, their presence would indicate that the peritectic limit at 2 per cent is too high and that Ruhrman and Schmidt may be more nearly correct.

L. W. Ball.—May I comment on the last speaker's remarks? I believe the X-ray micrograph method may be more suitable than the polishing and etching method in this case, because of the extremely favorable difference in the X-ray absorption of the constituents.

L. W. Kempf.—I wonder if anybody tried to fit these data to the equation or fit the equation to these data, whichever you please, which Fink and his colleagues used with such great encouragement on the aluminum system. Those equations worked particularly well in systems of this kind where solubilities are small.

J. B. Hess.*—Mr. Kempf refers to plotting the solubility curve on scales of the reciprocal of the absolute temperature against the logarithm of the mol fraction of alloying element. Such plots have been found to yield surprisingly straight lines when the crystallizing phase is a pure element or compound.

I have plotted Tiner's data and also those of Grogan and Haughton in this manner. Neither yield good straight lines. Tiner's data are decidedly curved in the direction, and to a degree, indicative of wide solid solubility in the crystallizing phase, while the data of Grogan and Haughton seem to be curved slightly, but consistently, in the opposite direction.

N. Tiner (author's reply).—The question raised by Mr. Ball—how to distinguish the suspension of very fine particles and a true solution—is of major importance. R. Mitsche[8] and other workers have attempted to detect the presence of very finely divided inclusions in cast-iron melts by their influence upon the course of crystallization. The author has undertaken a series of experiments on superheating of magnesium alloys.[9] It can be noted here that when magnesium alloys are superheated to about 850°C. in a graphite crucible, and then the crucible is taken from the furnace, cooled in air to 700°C. and immediately poured into graphite molds kept at 300°C., the following observations can be made.

1. Magnesium-aluminum alloys (9 to 10 per cent aluminum) do not show any appreciable grain refinement by superheating when prepared from extremely pure materials.

2. The addition of about 0.2 to 1.0 per cent manganese to the above alloys produces considerable grain refinement by superheating. It can be noted here that the presence of iron in magnesium-aluminum alloys is also im-

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[8] R. Mitsche: The Flotation of Nonmetallic Inclusions in Molten Metals. *Carnegie Schol. Memoirs*, Iron and Steel Inst. (1934) 23, 65.

[9] N. Tiner: Studies on Superheating of Magnesium Alloys. To be published in *Metals Technology*, 1946.

portant in producing grain refinement by superheating.

3. The effect of superheating is progressively but completely neutralized by holding the melts increasing periods of time at 700°C. before pouring.

Based on these observations, supported by many others, and on the present work, it can be said that solid manganese particles are dissolved in molten magnesium-aluminum alloys by superheating. During subsequent cooling they are precipitated in dispersed form (presumably as compound), and these fine particles exerted an inoculating action on the crystallization of the base alloy (which occurs at the lower temperature), and thus caused grain refinement. When the melt stands for too long at 700°C. before pouring, the present work shows that the excess manganese sinks to the bottom of the crucible, and since the grain refinement caused by the inoculating action of manganese is completely eliminated, one may ascertain that the amount of fine suspended particles left in the melt is negligible.

Pure magnesium containing large amounts of manganese does not show any appreciable grain refinement by superheating. This may be explained by assuming either that the alpha manganese, first separated from the melt as fine particles, has no appreciable inoculating action on the crystallization of the base alloy (magnesium-manganese solid solution), or that it has large growth rate and the few nuclei first formed grow rapidly into comparatively large particles. In the latter case the melt does not have fine suspension.

From this it follows that the solubility of manganese in liquid magnesium containing 7.5 to 8.0 per cent aluminum is definitely a true solubility. In the case of pure magnesium there may be some doubt, but since during crystallization processes large crystals usually tend to grow at the expense of their smaller neighbors if a sufficiently long period of time is allowed, and since practically the same composition is obtained both going up and coming down in temperature, it is reasonable to assume that a true equilibrium solubility is residing.

The Hardness of Silver-antimony Solid Solutions'

By R. M. Treco* and J. H. Frye, Jr.,* Member A.I.M.E.

(Cleveland Meeting, October 1944)

One of the chief hindrances to an understanding of the hardness of solid solutions is the sparsity of suitable hardness data. There is great need of a large body of hardness data obtained from many different alloys of high purity by identical testing methods and corrected to correspond to a single grain size. A considerable amount of such data has been obtained by means of the Meyer analysis on copper-rich and silver-rich solid solutions. There are enough of these data to permit comparison of numerous alloys at equal solute concentration in these two solvents, but only in a few cases is it possible to construct hardness-concentration curves for any given alloy. Therefore additional hardness work on most of these alloys is desirable.

The primary solid solutions of silver with cadmium, indium, tin, or antimony as solute are of special interest, since all elements are from the same period of the periodic table and since, as shown previously,[1] the hardening effect of equal percentages of these solutes is proportional to the lattice expansion produced by them. This paper presents the relation between hardness and concentration in the silver-antimony system from very dilute to nearly saturated solutions of antimony in silver.

Experimental Procedure

Alloys were made from silver, 99.99 per cent pure, and antimony, 99.975 per cent pure. Silver and antimony were placed in graphite crucibles that had an ash content of less than 0.75 per cent. These metals were melted and allowed to solidify in a vacuum, which, after melting was complete, was usually equivalent to 3 mm. of mercury. A high-frequency furnace was used.

The ingots so obtained were worked and annealed to lessen segregation and to control grain size. Annealing was done in evacuated and sealed glass tubes.

Hardness measurements on specimens from these ingots were by means of the Meyer analysis.[3,4] Using a 4-mm. ball, impressions were made under seven loads from 25 to 400 kg. The diameter of impression made under each load was measured. This enabled calculation of the constants in the well-known formula of Meyer.

$$L = ad^n$$

where L = load,
d = diameter of impression,
a = a constant,
n = a constant

The Meyer hardness is defined as

$$P = L/(\tfrac{1}{4}\pi d^2)$$

or

$$P = 4ad^{n-2}/\pi$$

Meyer hardnesses corresponding to $d = 1$ and to $d = 4$ are of especial interest, since the first corresponds to comparatively slight plastic deformation and the second to the maximum plastic deformation producible by penetration of the ball. These

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* Lehigh University, Bethlehem, Pennsylvania.

[1] References are at the end of the paper.

are defined by the equations

$$P_a = 4a/\pi \qquad (d = 1)$$
$$P_u = 4a(4)^{n-2}/\pi \qquad (d = 4)$$

Values of both P_a and P_u are reported, but attention is devoted principally to P_u, because it can be measured with far greater accuracy than P_a. P_u is called the ultimate Meyer hardness.

All equipment used in these tests was carefully calibrated. This, together with the experimental procedure described briefly here, has been described in detail in an earlier publication.[2]

After the measurement of hardness had been completed, chemical analyses for both antimony and silver were made on each specimen. Material for these was taken from the region of the hardness impression. In addition, oxygen analyses were made on several specimens.

TABLE 1.—*Hardness and Grain-size Measurements and Chemical Analyses*

Alloy No.	Antimony, Wt. Per Cent	Antimony, Atomic Per Cent	Grains per Sq. Mm.	Grain-boundary Area, Sq. Mm. per Cu. Mm.	n	P_a, Kg. per Sq. Mm.	P_u, Kg. per Sq. Mm.
T-11	0.60	0.532	115.0	32.2	2.549	22.33	47.84
T-12			92.6	28.9	2.543	22.59	47.95
T-13	0.74	0.671	18.0	12.7	2.596	20.04	45.79
T-23	0.00	0.000	2.0	4.24	2.521	20.56	42.34
T-24	0.00	0.000	35.1	17.8	2.566	20.79	45.58
T-31	2.86	2.541	310.8	52.9	2.540	28.57	60.37
T-32	2.44	2.171	157.6	37.7	2.669	22.38	56.60
T-41	4.75	4.229	95.6	29.3	2.634	27.10	65.28
T-42	4.66	4.148	81.1	27.0	2.656	26.12	64.83
T-51	0.00	0.000	26.3[a]	15.4	2.639	17.86	43.24
T-52	0.00	0.000	34.8	17.7	2.604	19.67	45.59

[a] Duplex grain size.

TABLE 2.—*Oxygen Analyses*

Sample No.	Approximate Antimony Content of Alloy, Wt. Per Cent	Oxygen Content of Alloy, Wt. Per Cent, 1[a]	Oxygen Content of Alloy, Wt. Per Cent, 2[a]
T-21	0	0.004	0.000
T-5	0	0.000	0.001
T-12	0.7	0.004	0.004
T-4	4.7	0.011	0.015

[a] Check determinations.

Grain-size measurements were made on each specimen. Specimens were cut in half through the hardness impression and measurements were made just beneath the impression. At least 150 grains were counted unless the grain size was too large for this to be feasible.

RESULTS

The results obtained through hardness and grain-size measurements and chemical analyses are presented in Table 1. Results of oxygen analyses are found in Table 2.

The ultimate Meyer hardness P_u depends primarily upon the concentration of antimony and to a lesser degree on the variation in grain size in the individual specimens. Before the effect of solute concentration on hardness can be determined precisely, it is necessary to correct the individual hardness values for grain-size variations. This must be done by a method of approximation, since specimens from the same ingot differ slightly in concentration because of segregation.[1]

All ultimate Meyer hardness figures were corrected to correspond to a standard grain size of 59 grains per sq. mm., as in earlier work.[1] This was done by assuming a linear relation between hardness and grain-boundary area. The latter is defined by the formula:

$$GBA = 3\sqrt{g}$$

where GBA is the grain-boundary area and g is the number of grains per unit area.[6] The values of P_u corrected to this standard grain size are listed in Table 3.

TABLE 3.—*Values of Ultimate Meyer Hardness Corrected to Standard Grain Size*

ATOMIC PER CENT SB	P_u, KG. PER SQ. MM.
0	46.9
0.53	46.6
2.17	54.7
4.15	64.7

These corrected results may be compared with previous work on silver alloys done in England,[1] with the same experimental procedure except that the alloys were not vacuum melted. There the ultimate Meyer hardness of 99.99+ per cent Ag was found to be 44.1 kg. per sq. mm. and that of 2.11 atomic per cent Sb was found to be 52.5 kg. per sq. mm. In the present work, the hardness of silver of the same nominal composition (99.99 per cent) was found to be 46.9 kg. per sq. mm., while that of silver with 2.11 atomic per cent Sb was found by interpolation to be 54.4 kg. per sq. mm.

The absolute hardness values of the present work are higher than those obtained in England, but the hardness increase produced by 2.11 atomic per cent Sb is the same in both instances within previously indicated limits of experimental error,[1] and increase in hardness produced by the solute is the primary concern of this work. The absolute values may differ because of differences in the impurities present in the two kinds of silver tested, since the equipment in each case was carefully calibrated, and since the hardness increase produced by antimony is the same.

RELATION BETWEEN HARDNESS AND PLASTIC DEFORMATION

It is never possible to determine values of P_a, the hardness corresponding to a 1-mm. impression, with anything like the accuracy obtainable for P_u, the hardness corresponding to a 4-mm. impression. For this reason values of P_a have not been corrected for grain size. Reference to uncorrected values of Table 1, however, leads to the conclusion that the hardening effect of antimony is greater for P_u than for P_a. Since P_u corresponds to a more severe plastic deformation than P_a, this indicates that the hardening effect of antimony in silver is strongly dependent on work-hardening and increases with plastic deformation over the range of deformation considered here. This is in agreement with earlier work.[1]

RELATION BETWEEN HARDNESS AND CONCENTRATION

Table 3 lists ultimate Meyer hardness values for pure silver and for silver containing a maximum of 4.15 atomic per cent Sb. The precise solubility limit of antimony in silver at room temperature is not known, but it is probably not greatly in excess of 4.15 atomic per cent. Thus the data at hand cover the range from pure silver to near the saturation limit of antimony in silver.

Increase in ultimate Meyer hardness has been plotted against composition in Fig. 1 for silver-antimony alloy and for other solid solutions to be discussed later. Each alloy point has been surrounded by a rectangle. It is believed that the points are accurate within the limits indicated by the rectangles. The relation between hardness and composition is linear between 0.5 and 4 atomic per cent Sb to well within experimental error.* The hardness of silver and of silver containing 0.53 atomic per cent Sb agree within limits of experimental error. Thus the addition of 0.53 atomic per cent Sb to silver that is 99.99 per cent pure produces no measurable increase in hardness, but larger additions produce a marked increase. This effect is discussed below.

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* Since there is a linear relation between concentration and lattice parameter for these alloys, essentially the same curve would be obtained if hardness were plotted against lattice parameter.[7]

Effect of Oxygen

Any study of the effect of solute additions on the hardness of a solvent metal should deal with solvent metal and binary alloys that are absolutely pure. In practice impurities are certain to be present, however, and it can only be hoped that their hardening effect, if serious, will be the same in the solvent and all the alloys. Oxygen is one impurity that is almost certain to be present, but which may be present in very different concentrations in solvent and solid solution if the solute acts as a deoxidizer.

It has been shown that the oxygen content of the specimens used here actually increases with concentration of antimony (Table 2). Handy and Harman, in making oxygen analyses by the hydrogen method, found a much severer grain-boundary attack in the 4 per cent Sb alloy than in pure silver. They attributed this to reduction of oxides of antimony that had precipitated in the grain boundary. That an oxide of antimony forms is suggested by other data. Frye and Hume-Rothery found a very definite precipitate in a 5 per cent Sb alloy that had not been vacuum melted. It was shown that this precipitate was not a second antimony-silver phase.[8] In view of the increase in oxygen content that has been shown to accompany increasing concentration of antimony, this second phase must be assumed to be an oxide, probably of antimony.

The formation of an oxide of antimony might mean that silver and silver containing 0.53 atomic per cent Sb would have the same hardness. In the first place, the removal of antimony from solid solution could have a softening effect. If the amount of antimony so removed were roughly equal to the oxygen content, however, the softening effect would be negligible. It is unlikely, therefore, that this can account for the absence of hardening. Second, the antimony may remove oxygen from solid solution or from some other condition in the silver that produces a hardening effect. Thus the solid solution hardening effect of the solute might be balanced completely by the softening effect due to removal of oxygen from solution or other condition in the solvent. It is possible that this accounts for the absence of hardening by 0.53 atomic per cent Sb.

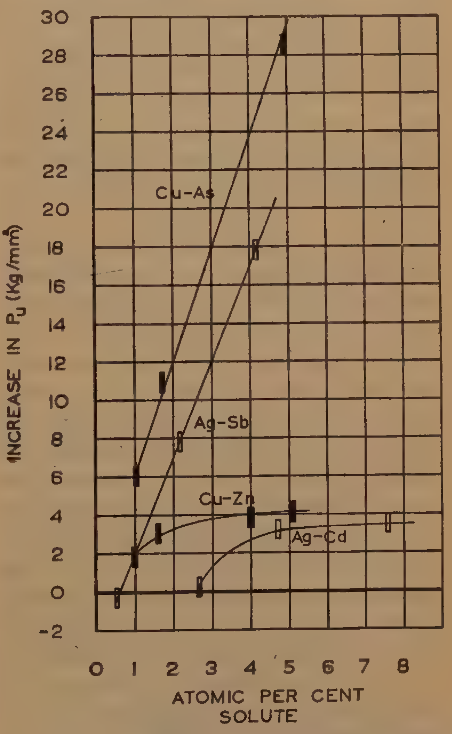

FIG. 1.—VARIATION IN INCREASE IN ULTIMATE MEYER HARDNESS WITH COMPOSITION OF ALLOY.

COMPARISON WITH OTHER ALLOYS

A comparison of the hardness concentration relation in this system with those in the solid solutions Cd-Ag, Zn-Cu, and As-Cu, is of especial interest, for three reasons: (1) accurate ultimate Meyer hardness data are available on all four alloy systems; (2) the hardening effect of equal concentrations of solute in either silver or copper is proportional to the lattice expansion produced by the solute; (3) both solute and solvent in each alloy are from the same period of the B subgroups of the periodic table. Furthermore, Cd and Zn are both group II B elements while Sb and As are both group V B elements.

In Fig. 1 increase in ultimate Meyer hardness has been plotted against concentration for all of these alloys. Small additions of cadmium* or antimony to silver produce little or no hardening. Appreciable hardening begins at a much lower concentration of antimony, as might be expected from the much greater lattice expansion of silver produced by it. Unfortunately, no ultimate Meyer hardness data are available on very dilute copper alloys. Brick, Martin, and Angier,[6] however, have shown that dilute binary solid solutions with copper as solvent and with zinc, nickel, manganese, aluminum, silicon, arsenic, or magnesium as solute have a smaller increment in Vickers hardness than copper after 10 per cent reduction by cold-rolling.

At higher concentrations the curves of Fig. 1 are strikingly similar for the analogous copper and silver alloys. The relation between hardness and concentration is linear to well within experimental error for both Sb-Ag and As-Cu. For Cd-Ag and Zn-Cu, the curves indicate a rapidly decreasing rate of hardening with concentration. Antimony and arsenic produce several times as great an expansion of their solvent lattices as do cadmium and zinc, and this may account for the difference in shape of these two sets of curves.

SUMMARY

The relation between hardness and concentration in the system silver-antimony has been determined over the range from very dilute to nearly saturated solutions of antimony in silver. It is found that 0.53 atomic per cent Sb can be added to silver containing 0.001 per cent oxygen without any measurable increase in hardness. At higher concentrations there is a linear relation between hardness and concentration of antimony. It is not clear whether the absence of hardening by 0.53 atomic per cent Sb is the result of the presence of impurities in the silver. It is probably safe to conclude that the initial slope of the hardness concentration curve is small even in the absence of impurities but increases rapidly to reach a maximum, which is constant to very near the solubility limit.

The effect of cadmium in silver is somewhat similar but the slope of the curve increases much less rapidly with concentration, probably because of the much smaller lattice expansion produced by this element, and at higher concentrations the slope passes through a maximum and then decreases.

Similar phenomena are shown to occur among copper solid solutions.

ACKNOWLEDGMENTS

The authors wish to thank Handy and Harman and Mr. John L. Christie, of that company, for making all oxygen analyses reported in this paper, and for helpful comments on the work.

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* Silver-cadmium hardness values are taken from the work of Frye and Hume-Rothery.[1] They measured the ultimate Meyer hardness of 99.99+ per cent pure silver and vacuum-melted spectroscopically pure silver obtaining 44.1 and 42.8 kg. per sq. mm., respectively. Oxygen analyses have now been obtained on these two silvers. Check analyses gave 0.000 and 0.003 per cent oxygen on the 99.99+ per cent pure silver. For the vacuum-melted spectroscopically pure silver, values were 0.000 and 0.001 per cent oxygen. Average values are 0.001 and 0.002 per cent, respectively, and these figures agree within limits of experimental error. It is not certain whether the measured difference in hardness is the result of difference in content of oxygen or of other impurities. Values in Fig. 1 for Ag-Cd are based on the hardness of the 99.99+ per cent pure silver, since cadmium was added to this silver to form the solid solutions.

They are grateful to Baker and Co., Inc., and to Mr. Frederic E. Carter, of that company, for supplying the silver used.

The antimony used in this work was kindly furnished by The Belmont Smelting and Refining Works through the courtesy of Mr. Robert V. Henning.

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The Constitution of the Gold-germanium System

BY ROBERT I. JAFFEE,* JUNIOR MEMBER, EUGENE M. SMITH,* JUNIOR MEMBER, AND
BRUCE W. GONSER,† MEMBER A.I.M.E.

(New York Meeting, February 1945)

THERE has been little investigation of the gold-germanium binary alloys. Haughton[1] does not mention any work on the system. In a review article commemorating the fiftieth anniversary of the discovery of germanium, E. Einecke[2] mentioned a gold-germanium eutectic at 24 atomic per cent Ge (10.4 weight per cent) melting at 359°C., but did not give the source of his information. From measurements of electrical conductivity, J. O. Linde[3] estimated that at least 0.6 weight per cent germanium is soluble in gold.

The recent availability of germanium in this country in commercial quantities has led to interest in its properties and its alloys. This study is part of a program of investigation on germanium alloys; work on ternary alloys involving germanium and gold will be reported later.

In this investigation, the composition and melting point of the Au-Ge eutectic reported by Einecke has been found to be substantially correct. Eutectic composition has been placed at 12.0 per cent germanium, however. An alloy of 10.4 per cent Ge, Einecke's value, was found to have a few gold dendrites in it. The eutectic temperature has been determined as 356.0 ± 0.5°C., slightly less than the temperature of 359°C. reported by Einecke. The liquidus curves and the solid solubility of germanium in gold have been determined, and are shown in Fig. 1.

MATERIALS AND ALLOYING

The germanium used in this investigation was prepared by the Eagle-Picher Lead Co. from pure germanium oxide, by reduction in clay crucibles with sodium cyanide. The regulus is quite pure, assaying over 99.9 per cent Ge. High-purity gold obtained from Handy and Harmon was used. Alloying was carried out in graphite crucibles in an atmosphere of purified hydrogen. The temperature was brought up to 1050° to 1100°C., and the metal was allowed to freeze in the crucible. Prepared in this way, the gold dendrites in hypoeutectic alloys were somewhat segregated at the bottom and sides of the ingot, and on the hypereutectic side the lighter primary germanium tended to gather at the top. Most of the alloys were made from virgin metal. Low-germanium heats were made by alloying pure gold with the eutectic. Melting losses were consistently a few milligrams or less, and the composition could safely be taken from the intended analysis. The 30 per cent and 50 per cent germanium heats for thermal analysis were made in part from remelted higher germanium heats, and they may be off composition as much as one per cent. Because of the high cost of materials, the weight of heats for thermal analysis were 15 to 20 grams and heats for metallographic, X-ray, and hardness specimens were 2 to 4 grams.

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[1] References are at the end of the paper.

THERMAL ANALYSIS

With heats of 15 to 20 grams weight, it was found that simple cooling curves gave the most reproducible results. Attempts to use controlled cooling rates using a differential thermocouple and a controller with reversed connections were not successful, principally because of variation in cooling rate caused by the intermittent control current. A satisfactory method of handling the small melts was to hold the metal in a closed, thin-walled, 10-mm. Vitreosil or Pyrex tube. A Vitreosil thermocouple protection tube with its closed end drawn out about 1 in. and down to half thickness fitted loosely in the melting tube, the drawn out tip projecting into the melt for about 0.75 in. A hole in the melting tube about 1.5 in. above the metal allowed hydrogen to pass from the furnace over the melt. The thermal analysis was run in a vertical tube furnace, which cooled

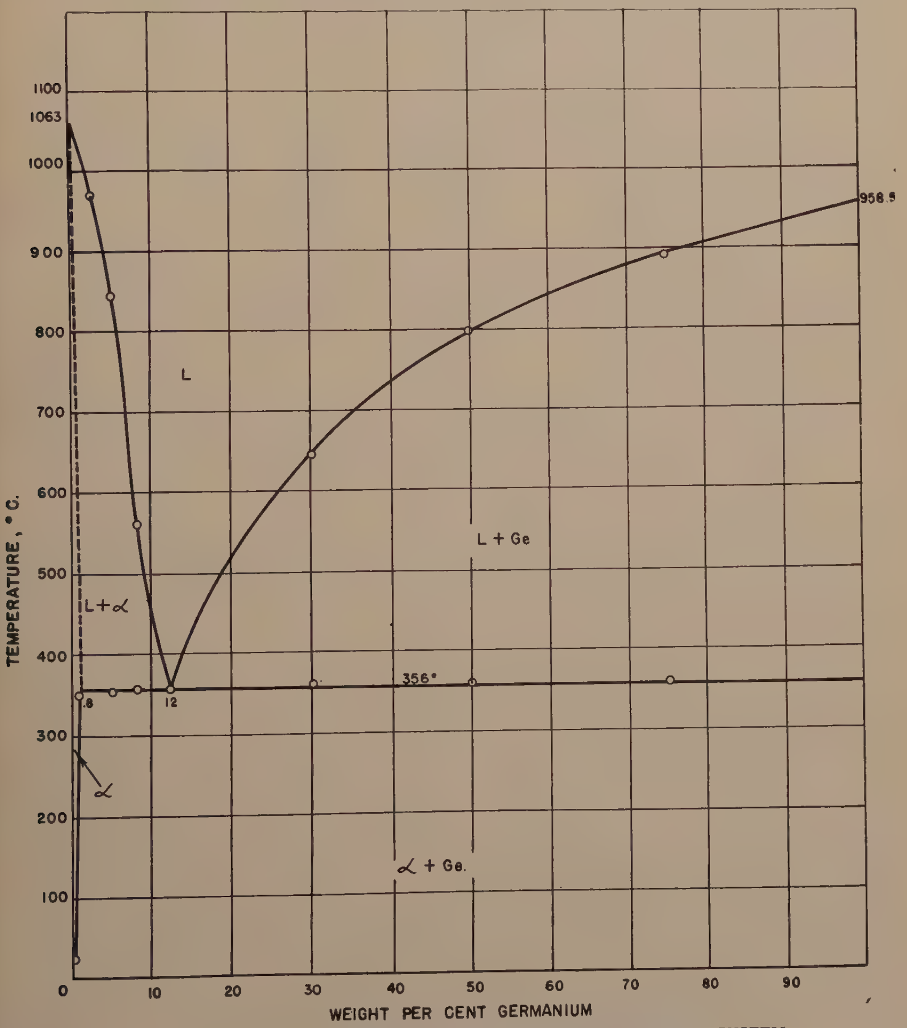


FIG. 1.—CONSTITUTIONAL DIAGRAM OF THE GOLD-GERMANIUM SYSTEM.

at a rate of 2° to 4°C. per min. at low temperatures and 4° to 8°C. per min. at high temperatures. A 24-gauge iron-constantan thermocouple, checked frequently at the lead, antimony, and silver points, was used for the temperature measurement.

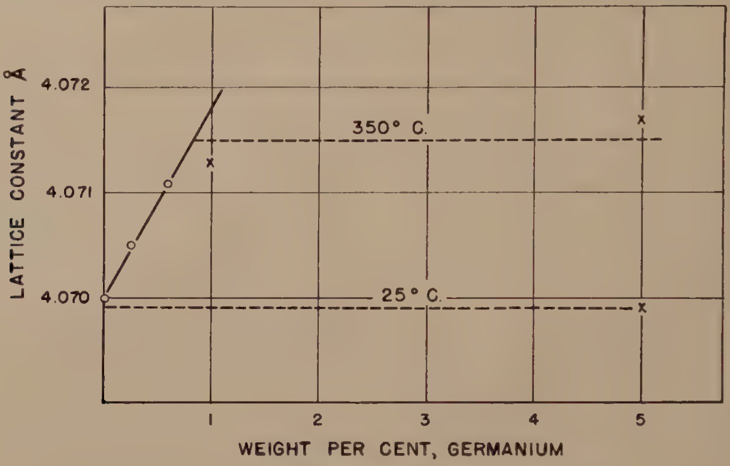


FIG. 2.—X-RAY DETERMINATION OF SOLID SOLUBILITY.

The liquidus arrests on the gold side of the eutectic were slight because of the steep liquidus line and the long mushy range, but the arrests were quite definite and reproducible. Undercooling occurred chiefly at the liquidus arrests on the germanium side, particularly when the eutectic solidified, but from the course of the curves before and after the undercooling the true arrest temperature could be obtained. The thermal analysis data are given in Table 1. The liquidus temperatures are considered accurate to ±15°C., with the probability that they would be low if in error. The eutectic temperature was determined many times on the pure eutectic and is considered accurate to ±0.5°C.

TABLE 1.—*Thermal Analysis*

Germanium, Weight Per Cent	Liquidus Temperature, Deg. C.	Solidus Temperature, Deg. C.
0		1063.0[a]
2.5	969	
5	844	354
8	560	356
12		356.0
30	646	361
50	797	360
75	891	359
100		958.5[a]

[a] Values taken from the International Critical Tables.

SOLID SOLUBILITY

The X-ray method of determining solid solubility was used and the results obtained were checked metallographically. Specimens containing 0, 0.25, 0.60, 1.0, and 5.0 per cent germanium were prepared, and homogenized by alternate cold hammering and soaking at 350°C. Finally they were slowly cooled to room temperature. Filings were taken from the homogenized alloys, sealed in evacuated glass tubes, and annealed at 350°C. in a vertical quenching furnace for 1 to 2 days. They were drastically quenched in water, a ramrod being used to eject the specimens rapidly. Solid pieces of the homogenized ingot, measuring about 2 mm. square, were soaked in a salt bath at 350°C. for 147 hr. and water-quenched to provide a metallographic check on the X-ray results. Back-reflection diffraction patterns were taken using copper radiation and a Debye-Scherrer camera with a Van Arkel setting, and precise lattice constants were calculated from the patterns. A diffraction pattern on filings taken from the homogenized slow-cooled 5 per cent Ge alloy was taken to determine the solid solubility at room temperature. These filings were strain-annealed by heating at 300°C. for a few minutes.

Table 2 gives the results of the X-ray and metallographic work; lattice constants are plotted in Fig. 2. The three points corresponding to one-phase alloys fall on a straight line. The horizontal line corresponding to saturation is drawn between the points for the two-phase 1 Ge and 5 Ge alloys, which should have had the same lattice constant. Solid solubility of germanium in gold is indicated by the data to be about 0.8 weight per cent at 350°C. and practically zero at room temperature. In order to check the zero solubility at room temperature, alloys of 0.2, 0.4, 0.6, 0.8, and 1.0 per cent Ge were made up, melted in hydrogen, and furnace-cooled from the liquid state to room temperature. All of the alloys show the presence of patches of eutectic but there were only a few very small patches in the 0.2 per cent Ge alloy. It may be concluded that the solubility of germanium in gold at room temperature is less than 0.1 per cent.

No attempt was made to determine the solid solubility of gold in germanium, but it is believed to be negligibly small.

MICROSTRUCTURE

From a microscopic study, the eutectic composition has been placed at 12.0 per cent germanium. The extreme fineness of the eutectic structure is most striking; it is shown in Fig. 6 for a 10 per cent Ge alloy slowly cooled from the alloying temperature. The structure is resolved at 1000 diameters, and appears to be composed of angular germanium particles in a gold matrix. Undercooling apparently has a part in promoting the fine structure, since normally slow freezing leads to coarse eutectic structure. In line with this, it is worth noting that the eutectic structure was fine grained in hypoeutectic alloys and in the pure eutectic, both of which undercooled severely, while the coarse eutectic in hypereutectic alloys undercooled to only a normal degree. The fine grain in the eutectic structure in alloys on the gold side of the eutectic is shown in Figs. 3 to 6. Long holding at 350°C. appears to coarsen the eutectic structure somewhat; Fig. 4, for a 1 per cent Ge alloy soaked at 350°C. for 147 hr., shows this tendency, and also illustrates the resolution of eutectic on long holding at 350°C. The primary germanium particles in hypereutectic alloys is particularly massive, and pieces may extend from one end of the ingot to the other. Figs. 7 and 8 show typical examples of hypereutectic alloys.

TABLE 2.—*Data for Solid Solubility*

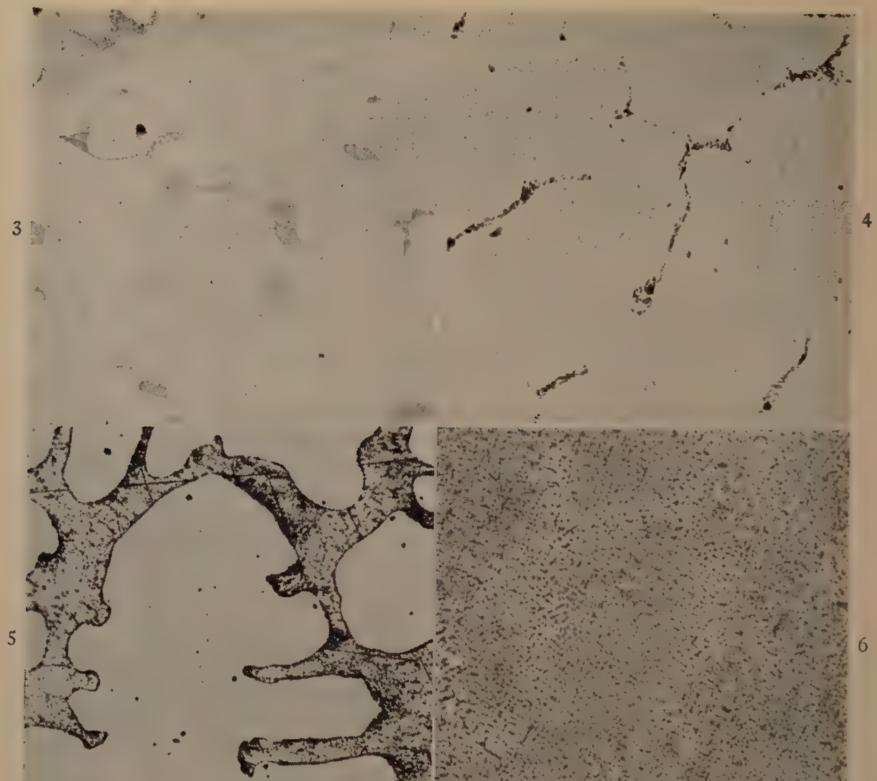
Germanium, Weight Per Cent	Microstructure, Annealed at 350°C.[a]	Heat-treatment of Powder, Hr. at 350°C.	Lattice Constant, Å.
0	One phase	Strain-annealed	4.0700
0.25	One phase	41	4.0705
0.60	One phase	48	4.0711
1.0	Two phase	26	4.0713
5.0	Two phase	67	4.0717
5.0	Two phase	None[b]	4.0699

[a] Specimens annealed 147 hr. and water-quenched.
[b] Filings taken from slowly cooled ingot, and strain annealed for a few minutes at 300°C.

Germanium appears in the polished unetched microstructure as an angular blue-gray phase, resembling free silicon. Etching with aqua regia appears to have little effect on the structure. It was found that relief polishing with 600 Alundum on a Sylvite cloth gave the best metallographic results.

PROPERTIES

Germanium increases the hardness and strength of gold up to the eutectic composition, but brittleness increases correspondingly. Up to about 5 per cent germanium the alloys are fairly malleable. At higher germanium contents the alloys become too



Figs. 3–8.—Gold-germanium alloys.
Fig. 3. 1 per cent Ge, as cast. Unetched. × 100.
Fig. 4. 1 per cent Ge, annealed 147 hr. at 350°C. Unetched. × 100.
Fig. 5. 5 per cent Ge, as cast. Unetched. × 75.
Fig. 6. Eutectic, as cast. Unetched. × 1000.
Fig. 7. 30 per cent Ge, as cast. Unetched. × 50.
Fig. 8. 75 per cent Ge, as cast. Unetched. × 50.

brittle to be deformed much. The tensile strength of the eutectic alloy, as determined with a flat tensile bar cast in a graphite mold, was 55,600 lb. per sq. in., and the elongation between 1-in. gauge marks was negligibly small. Vickers pyramid hardness of cast gold-germanium alloys were measured using loads of 1 and 2 kg. The results are plotted in Fig. 9. The hardness increases up to the eutectic, and falls off in the hypereutectic field.

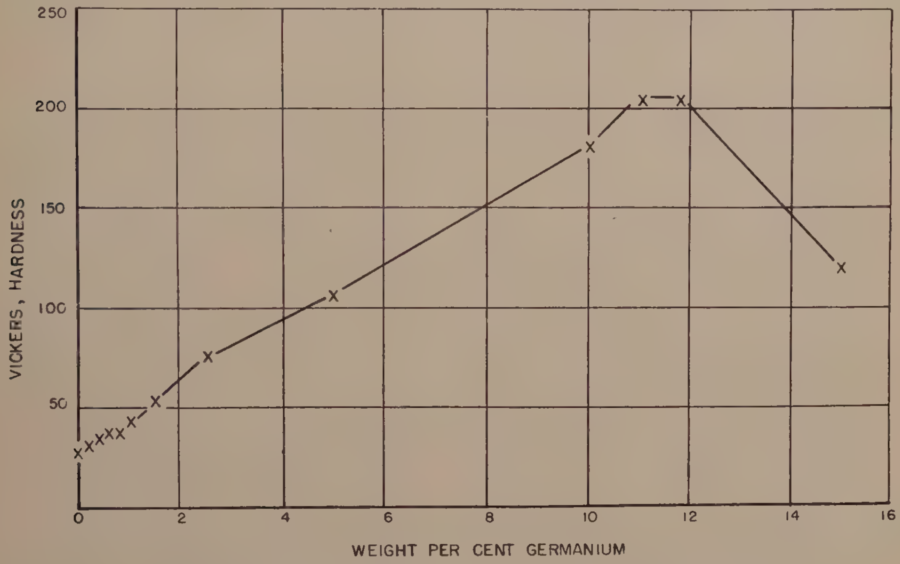


FIG. 9.—VICKERS HARDNESS OF CAST GOLD-GERMANIUM ALLOYS.

Gold-germanium alloys retain their gold color up to the eutectic composition. Large primary germanium particles give the hypereutectic alloy a gold-gray mottled appearance. Rapid cooling accompanying chill casting does not appear to discolor the eutectic alloy. Loskiewicz[4] noted that the structure of the gold-silicon eutectic (similar to the Au-Ge system in that there is a low-melting eutectic of 370°C. at 6 per cent Si) depends on the rate of cooling. With rapid cooling, the Au-Si eutectic structure was very fine and the color was almost white. It was possible to discolor the gold-germanium eutectic to a silver color only by pouring the molten alloy into water. The silver color was a surface effect, apparently caused by a germanium-rich layer freezing first when the molten alloy came in contact with the water. The normal gold color could be restored by heating gently in a Bunsen flame.

Pure germanium "sprouts" when it freezes[5] because of expansion during solidification. The binary gold-germanium eutectic alloy also sprouts, showing small ridges of metal on an otherwise smooth surface. When the eutectic alloy freezes in glass tubes, it cracks the glass. The alloy reproduces mold surfaces very well on casting, and it is thought that the expansion on solidification contributes to this property.

Density measurements on gold-germanium alloys were found to correspond quite closely with the values calculated from the density of pure gold and pure germanium.

A number of practical applications are suggested by these properties. For example, the hardness and good color of the hypoeutectic alloys may be of value in some types of jewelry; the drastic reduction in melting point and tendency to correct shrinkage by germanium additions to gold may be useful in dental work or precision castings; the low-melting eutectic suggests improved gold solders or the reduction in melting temperature of gold-containing alloys. Gold-base materials have been successfully soldered in the laboratory at a temperature of only 360° to 375°C., by using the eutectic alloy.

CONCLUSIONS

1. The system gold-germanium has been found to be eutectiferous, with a eutectic of 12.0 per cent germanium melting at 356°C.

2. Using X-ray, as well as metallographic means, the solid solubility of germanium in gold has been placed at 0.8 per cent at 350°C. and 0.1 per cent or less at room temperature.

3. Structure of the alloy at the eutectic and on the gold side was found to be fine, but it became very coarse on the germanium side of the eutectic.

4. Experimental densities coincided closely with density calculated from the constituents.

5. Expansion of the eutectic on freezing, as well as of alloys on the germanium side, was noted. Hardness and color values of the alloys have been reported, and applications in soldering jewelry and precision castings suggested.

ACKNOWLEDGMENTS

The authors are deeply grateful to the Eagle-Picher Lead Co. for permission to publish these results, and to E. W. McMullen, John Sommerville, and C. Tietig, of the same company, for helpful comments and excellent cooperation.

ADDENDUM

Since this paper was published, Owen and Robert[6] have reported more complete work on the alpha phase boundary of the gold-germanium system than is contained in this paper, and their results are shown in Fig. 10. The value of 0.8 weight per cent Ge in gold at 350°C., which we have found, is in good agreement with Owen and Robert's findings. Their value of the eutectic temperature, 363°C., is higher than ours, but they claim the value to be between 350°C. and 363°C., and did not use thermal analysis in the determination.

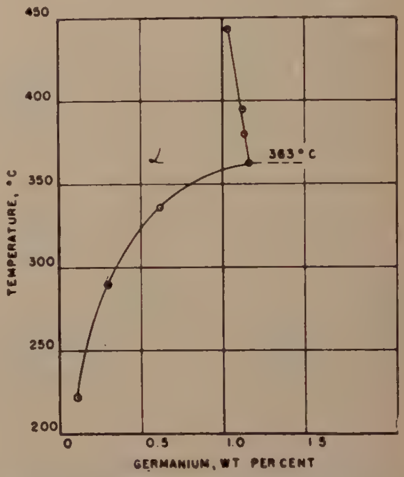


FIG. 10.—ALPHA PHASE BOUNDARY OF GOLD-GERMANIUM ALLOYS AFTER OWEN AND ROBERT.[6]

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Hydrogen Content of Electrolytic Manganese and Its Removal

By E. V. Potter,* E. T. Hayes,† and H. C. Lukens*

(New York Meeting, February 1945)

Large volumes of hydrogen are liberated at the cathode during electrolytic precipitation of manganese. Most of the gas escapes from the electrolyte, but a considerable amount may be entrapped in the manganese plate. Gas has been observed to escape from manganese melts in puffs that ignite at the surface. It has been reported that castings made with electrolytic manganese tend to rise in the molds; for this reason the manganese is often treated to remove hydrogen before the melt is made or it is premelted and used as cast manganese in making the alloys. The effect of hydrogen on the properties of manganese and its alloys is not known, but its effect on iron and iron alloys has been studied extensively.[1,2] The close relationship between iron and manganese suggests that hydrogen may have a similar effect on the properties of manganese and its alloys. The purpose of this investigation was to determine the amount of hydrogen or other gases in typical commercial electrolytic manganese sheet and to investigate ways of removing it most conveniently.

Apparatus

The apparatus used is shown schematically in Fig. 1. It consists of a chamber *A* in which the metal sample is placed, a vacuum or pressure gauge *B*, volume gauge *C*, vacuum pump *D*, hydrogen container *E*, auxiliary gas chamber *F*, and furnace *G*. The specimen chamber was made of two concentric quartz tubes. The outer one, *a*, connects with the closed gas system and is surrounded by the furnace *G*. A second tube, *b*, fits closely inside *a* and has a small end that projects into the space for the specimen and holds the thermocouple for measuring the temperature of the sample. The inner tube is joined to the outer tube outside the furnace, with rubber tape and sealing wax, to prevent gas leakage into or out of the closed system. This type of specimen container is loaded very easily and can be used several times if molten metal does not come in contact with the quartz.

An ordinary mercury manometer *B* is used to measure the pressure in the system. The volume gauge *C* is essentially another mercury manometer, but the volume of the column is much larger than normal and the height of the mercury can be varied by raising or lowering the well *H*. In this apparatus the tube had a volume of 100 c.c. for a 60-cm. length. For larger changes in gas volumes, auxiliary containers *F* were used to increase the volume of the system by known amounts. Valves were arranged so that these auxiliary containers could be filled from the system and evacuated by the pump as often as necessary to accommodate the increases in the volume of gas in the system. The furnace *G*, used to heat the samples, was equipped with an automatic temperature controller, which maintained the desired temperatures within ±5°C.

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METHOD

The experimental procedure was as follows: The complete system was evacuated and refilled with hydrogen until all the air was removed. It was then refilled with hydrogen to the desired pressure as indicated on manometer *B* (Fig. 1). The temperature was then raised in steps and held constant until equilibrium was reached, the height of well *H* being varied to maintain the desired pressure in the system as gas was liberated from the sample. The volume change and temperature at equilibrium were noted, and the temperature was changed to the next level.

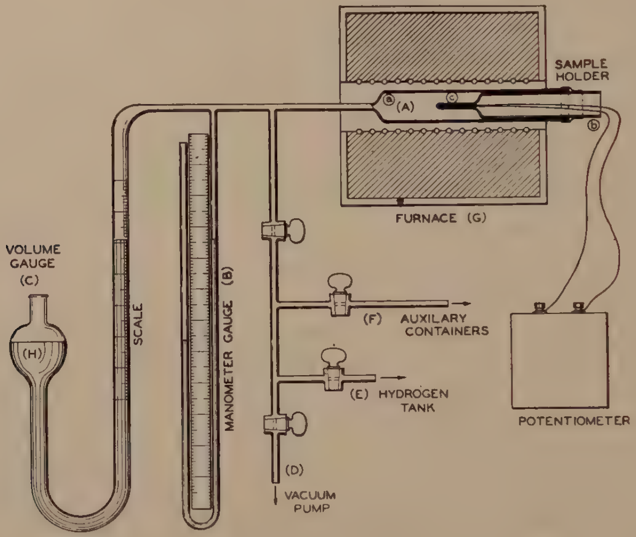

FIG. 1.—APPARATUS FOR DETERMINING GAS CONTENT.

The volume changes obtained in this way are greater than the volume of gas liberated from the specimen because the gas in chamber *A* expands as the furnace heats. The correction for this expansion was determined by filling chamber *A* with a volume of quartz equal to the volume of the metal sample and measuring the change in volume of the gas as the sample temperature was raised.

It was expected that the time required to reach equilibrium could be quite long and very indefinite, therefore two criteria for equilibrium were adopted. When samples crushed and sized to −14+48-mesh were used, a change in volume of less than 0.5 c.c. in 15 min. was considered to be sufficiently close to equilibrium, while in tests in which sheets of metal were used a change of 0.5 c.c. in 30 min. was taken as a standard.

PROCEDURE AND RESULTS

A series of tests was made to determine the temperature required to drive the maximum amount of gas from the metal and what effect pressure would have on the amount of gas liberated, and also its rate of liberation. The manganese used in these tests was produced at the Bureau of Mines pilot plant at Boulder City, Nev., and it was about three months old when the tests were made. The metal was crushed and sized to −14+48-mesh, and tests were run at pressures from 10 to 760 mm. of hydrogen and temperatures up to the melting point of manganese. In several runs the gas was sampled and analyzed to discover gases other than hydrogen that might be present in the metal.

A curve typical of the results obtained is shown in Fig. 2. Upon heating, very little gas is liberated up to 200°C., but at 300°C. a large volume is released. Heating to 400°C. releases a little more gas, but no further change occurs until 700°C. is reached. Above 700°C. hydrogen is reabsorbed; four definite breaks occur in the curve. They occur in the temperature intervals 720° to 738°C., 1082° to 1112°C., 1135° to 1146°C., and 1230° to 1255°C., and represent definite changes in hydrogen solubility corresponding to the transitions alpha to beta, beta to gamma, gamma to delta, and delta to melt, respectively.

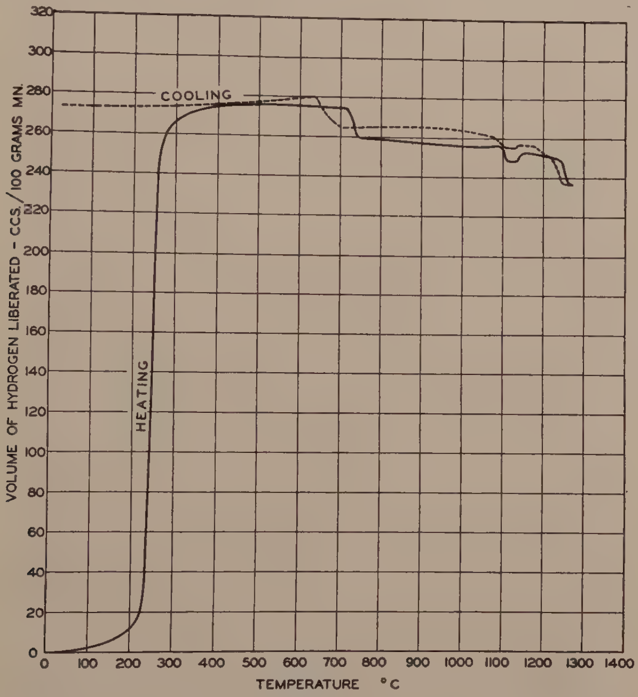

FIG. 2.—VOLUME OF HYDROGEN LIBERATED VS. TEMPERATURE.

On cooling, similar breaks occur in the curve at approximately the same temperatures, except for the change from beta to alpha, which on cooling takes place below 680°C. (These transitions will be discussed in a paper to be published later; since they have no bearing on the immediate problem, they warrant no further discussion in this paper.)

Below 600°C., about 7 c.c. of gas per 100 grams of metal is again reabsorbed. This represents true absorption of hydrogen by the metal and is very small compared with the 275 c.c. liberated on heating. Sieverts and Moritz[3] obtained similar results above 500°C.; below 500°C., they found that about 34 c.c. per 100 grams of metal was absorbed on cooling. In addition, they show the metal to contain in solution about 9 c.c. of hydrogen per 100 grams at 500°C. We made no attempt in this work to obtain hydrogen-free manganese nor to determine the actual hydrogen content of a sample. The volumes given represent only the changes in hydrogen content.

Obviously only a small volume of the 275 c.c. of gas liberated on heating to 500°C. represents truly absorbed gas; 241 to 268 c.c. must be adsorbed, entrapped, or present in the metal as a supersaturated interstitial solution. This gas represents 18 to 20 volumes relative to the metal, as compared with 25 volumes for iron.[1]

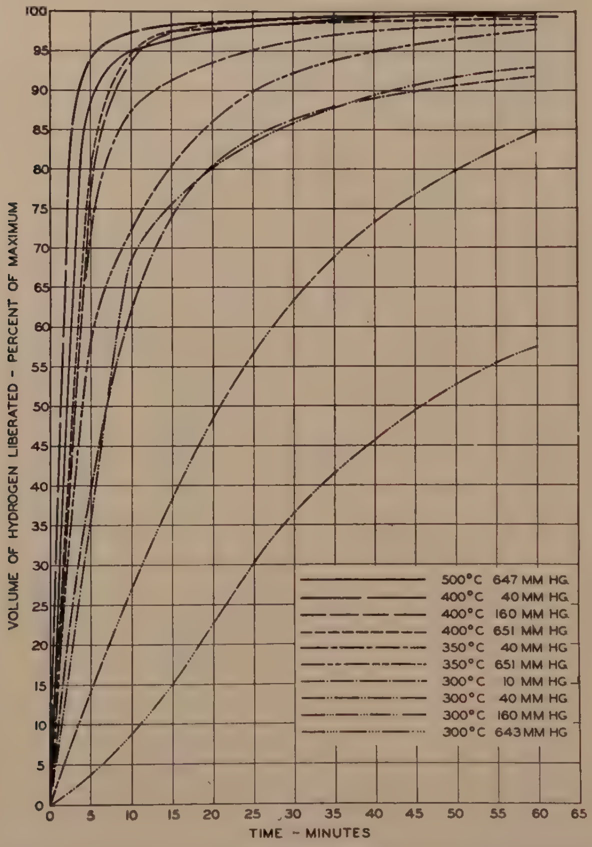

FIG. 3.—VOLUME OF HYDROGEN LIBERATED VS. TEMPERATURE.

The curves (Fig. 2) obtained at various pressures from 10 to 760 mm. of mercury are almost identical and show that heating to 500°C. will release the maximum volume of gas. In addition, there was no correlation between the volume of gas released at 500°C. and the pressure. The results indicate that wider variation exists between the volumes of gas in individual specimens than could be attributed to pressure differences. The only positive effect of pressure was to change the rate at which the gas was liberated. This will be discussed later. The average volume of gas released on heating to 500°C., as determined from 16 tests, was 253 ± 25 c.c., with maximum deviations of +56 and −78 cubic centimeters.

The analyses of the gas samples obtained on these runs showed it to consist principally of hydrogen and oxygen. The oxygen ranged from 0.3 to 0.7 per cent, and the remainder was hydrogen except for a small amount of CH_4.

Since the material used in the test was crushed, it had much more surface in a given volume than the original sheets and the rate of evolution of the gas should be greater. A second series of tests was made to determine the most practical temperature, pressure, and heating period for metal as it would be used industrially.

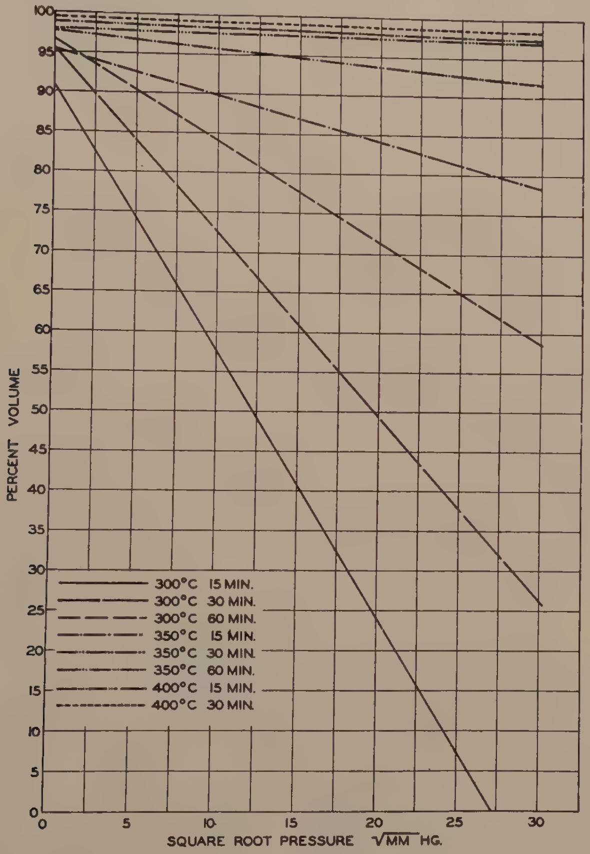

FIG. 4.—VOLUME OF HYDROGEN LIBERATED VS. TEMPERATURE.

Pieces of the original cathode sheet, about 1 by ½ by 0.05 in., were packed in the heating chamber as closely as possible. The system was evacuated and refilled with hydrogen as before and the samples were heated as rapidly as possible to the desired temperature. The volume of gas liberated at this temperature was determined at convenient time intervals until equilibrium was reached. The specimen was then heated to between 500° and 700°C. to remove any remaining gas, and was allowed to cool. As would be expected from the previous tests, the absolute volumes of gas liberated from the samples varied too much for direct comparison, so the results were expressed as percentages of the maximum amount that could be removed by heating to 500°C. The results obtained from these tests are shown in Fig. 3 and represent temperatures from 300° to 500°C. and pressures from 10 to 650 mm. (normal atmosphere pressure in this laboratory) of mercury.

The rate of liberation of hydrogen varies widely with temperature and pressure, but the temperature seems to be the more important factor. For example, the liberation is slower at 300°C. and 10 mm. than at 350°C. and 651 mm., and similarly, 350°C. and 40 mm. is slower than 400°C. and 651 mm. Temperatures of 300° and

350°C. are too low, and the results at 400° and 500°C. are very nearly the same.

In Fig. 4, the results have been plotted to show the amount of gas liberated in given time intervals as a function of the square root of the pressure. The effect of pressure is seen to be great at the lower temperatures but practically negligible at 400°C. for heating periods over 15 min., or 350°C. for a heating period of 1 hr. At atmospheric pressure, 97 per cent of the removable gas is liberated in 15 min. at 400°C., while at 40 mm. pressure the amount is increased only to 98 per cent. Considered solely on the basis of hydrogen removal, the additional 1 per cent would not warrant the use of the lower pressure with the attendant complications in the equipment.

Other factors must be considered, however, before the final selection of a processing temperature, pressure, and time is made; these results do not give all of the information required for an intelligent choice. All of these tests were made in an atmosphere of pure hydrogen but, in practice, it is more likely that the metal would be heated in air. At the temperatures indicated by the previous work as being desirable, manganese will react to a considerable extent with both the oxygen and nitrogen of the air. According to Mellor,[4] the metal can absorb 0.08 per cent N_2 at 400°C. and 0.37 per cent at 500°C., amounts that definitely are not negligible. Exactly how much oxygen and nitrogen could be tolerated in the metal is not known. The objective should be to adjust the pressure and temperature to give the best possible compromise between elimination of hydrogen and reaction with oxygen and nitrogen.

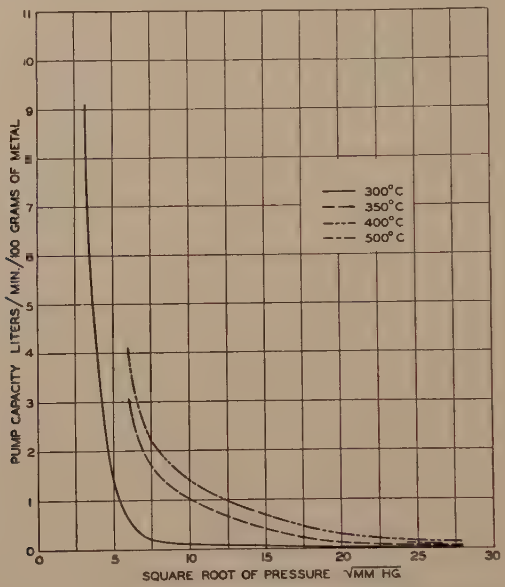

FIG. 5.—PUMP CAPACITY VS. SQUARE ROOT OF PRESSURE.

Several samples of manganese sheet were heated at atmospheric pressure (645 mm.) to 350°, 400°, and 500°C. for periods of 15 min. to 1 hr. When cool, they were placed in the sample chamber and tested to determine the amount of hydrogen remaining. Samples were then analyzed for nitrogen by a modified Kjeldahl method, using very dilute acid. The oxygen could not be determined directly but was estimated from the change in weight of the sample when heated in air, allowance being made for the hydrogen lost and the nitrogen absorbed. In addition, the appearance of the surface of the samples gives a fair qualitative measure of the amount of oxidation that has occurred. The results of these tests are shown in Table 1.

TABLE 1.—*Gas Content of Manganese Sheet*
PER CENT

Treatment	Hydrogen Removed	Hydrogen Removable (Fig. 3)	N_2	O_2
350° ¼ hr.	43.0	81.0	0.003	
350° ½ hr.	56.0	92.0	Nil	
350° 1 hr.	94.0	98.0	Nil	
400° ¼ hr.	91.0	97.5	0.03	
400° ½ hr.	95.0	98.5	0.04	
400° 1 hr.	97.0	99.3	Nil	
400° 1 hr.	97.0	99.3	0.01	0.03
500° 1 hr.	101.2	100.0	0.03	
500° 1 hr.	101.2	100.0	0.01	0.16

In every case except at 500°C., the volume of hydrogen removed is less than that indicated by Fig. 3, but approaches that volume as the treatment time is increased. The nitrogen content is also less than might be expected, especially at 500°C. These facts indicate that the oxide film on the metal surface probably interferes with the absorption of nitrogen and the liberation of the hydrogen, although the hydrogen can still be removed if sufficient time is allowed.

The nitrogen content is essentially the same for 15 min. or 1 hr. at either 400° or 500°C., indicating that 0.01 to 0.03 per cent is absorbed rapidly at first but further absorption is prevented by the oxide film that soon forms. The oxygen content increases with time, however, and is much greater at 500°C. than at 400°C. Good quantitative data are not available to substantiate this for each case, but the appearance of the metal surface indicates that this is true. At 350° and 400°C., the surface shows colors grading from very faint to rather intense and brilliant as the time and temperature increase. At 1 hr., however, and especially at 500°C., definite colors are replaced by a dull and stained appearance, indicating a relatively thick coat of oxide at this stage.

These results indicate that the hydrogen entrapped in electrolytic manganese can be removed effectively without heating the metal to over 500°C. or for longer than 1 hr., either in air or a nonoxidizing atmosphere, and at atmospheric pressure or in a partial vacuum. The removal of more than 100 per cent of the hydrogen by heating to 500°C. indicates that some gas was reabsorbed when the metal was reheated in a hydrogen atmosphere and shows that part of the gas, soluble in the metal at 500°C. and 650 mm. hydrogen pressure, was removed when the sample was heated in air under a hydrogen partial pressure of about 0.07 millimeters.

Another sample heated to 500°C. for 1 hr. in a vacuum showed the removal of 102.2 per cent of the hydrogen. The nitrogen content was 0.02 per cent. The oxygen content could not be obtained from actual measurements but the surface coloration indicated it to be less than 0.03 per cent.

The simplest treatment would be to heat the metal in air at atmospheric pressure. Optimum results are obtained by heating for 1 hr. at 400°C.; 97 per cent of the removable hydrogen will be driven off and the oxygen and nitrogen contents will not exceed 0.03 per cent. For ½-hr. heating period, the oxygen is less, but more hydrogen is left in the metal; in most cases, 0.03 per cent oxygen probably would not be detrimental to the metal or its alloys. Increasing the temperature to 500°C., however, would greatly increase the oxygen content and permit the removal of only 3 per cent more hydrogen. Any advantage from the removal of this additional amount of hydrogen would not offset the concomitant increase in oxygen content.

An improved product could be obtained if the treatment were made in a partly evacuated system. The improvement would be twofold because the smaller amount of oxygen in the atmosphere would reduce the formation of the oxide film and the hydrogen would be liberated more rapidly, reducing the time required for its removal. As the pressure is reduced, the time required would approach those shown in Fig. 3, and 97 per cent of the hydrogen could be removed in less than ½ hr. at 400°C. with a pressure of 40 mm. of mercury. In addition, the oxygen and nitrogen contents would be less than 0.01 per cent. In a good vacuum, the temperature could be raised to 500°C. without increasing the oxygen or nitrogen content to over 0.03 per cent for 1-hr. treatments. In this case, the removed hydrogen will be over 100 per cent (102.2) and part of the gas soluble at this temperature under a pressure of 650 mm. of hydrogen will be removed. This 2.2 per cent corresponds to approximately 5 c.c. of gas and (according to Sievert and Morris, the metal should contain a total of 9 c.c. of hydrogen in equilibrium at 500°C. and 650 mm. pressure) indicating that the absolute hydrogen content of the metal was 4 c.c. per 100 grams of manganese.[8]

A still better procedure would be to heat the metal in a nonoxidizing atmosphere. Hydrogen gas would duplicate the conditions under which the results in Fig. 3 were obtained but this would be hazardous and more expensive than air. A nitrogen atmosphere would eliminate the hazards but it would also be more expensive. The nitrogen content of the metal might reach 0.08 per cent at a temperature of 400°C. but the high solubility of manganese for nitrogen would prevent its liberation from the metal as a gas, so it would not cause trouble in making castings. Furthermore, there is evidence to show that nitrogen is beneficial to some alloys and increases their workability.

In order to determine the approximate capacity of a pump that would be required to remove the gas as it is liberated from the metal, the data shown in Fig. 4 were used to calculate the volume of hydrogen liberated per minute per 100 grams of manganese, and these data are plotted in Fig. 5 against the square root of the pressure for four temperatures. The pump capacities were calculated on the basis of the initial rate of liberation of the gas, and such pumps will maintain the pressure at the desired value or lower throughout the treating period. The average rate of liberation of the gas for the first 5 to 15 min. could be used for determining the pump capacities, and the requirements would be considerably lower, but if that were done the pressure would rise above the desired value during the interval used in the calculations and somewhat increase the necessary treatment time. In such cases the capacity could be reduced by a factor of 2 to 6, depending on the length of time used in determining the average rate. In addition, when the material is heated in air at atmospheric pressure, the rate of liberation is further reduced by another factor of 2 to 4. In any case, at 400°C. a small vacuum pump handling 10 liters per minute could remove the gas from 22 lb. of manganese at 645 mm. pressure, or 1 lb. of manganese at 40 mm. pressure. Since the pressures required are not low, pumps capable of high capacities but limited in ultimate vacuum would be entirely satisfactory and are readily available and reliable.

CONCLUSIONS

1. Approximately 250 c.c. of hydrogen is adsorbed or entrapped in 100 grams of electrolytic manganese.

2. This hydrogen can be effectively removed by heating the manganese to not over 500°C. for longer than 1 hr., either in air or an oxygen-free atmosphere, at atmospheric pressure or in a partial vacuum.

3. Heating to 400°C. for 1 hr. in air at normal pressure will remove 97 per cent of the removable hydrogen with the

absorption of not over 0.03 per cent of oxygen and nitrogen.

4. Shorter heating times are required at reduced pressures and correspondingly less oxygen and nitrogen are absorbed. Heating to 400°C. for less than ½ hr. is sufficient to remove 97 per cent of the removable hydrogen at 40 mm. pressure, and the oxygen and nitrogen contents will probably be less than 0.01 per cent.

5. Heating to 500°C. for 1 hr. in a vacuum will reduce the hydrogen content to less than the amount soluble at 500°C. and 650 mm. hydrogen pressure without increasing the oxygen or nitrogen content to over 0.03 per cent.

6. A product as free of hydrogen as desired, and containing no other inpurities not present in the original metal, can be obtained by heating in an atmosphere of some inert gas, or in hydrogen; heating in nitrogen may introduce as much as 0.37 per cent nitrogen into the metal.

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Substitute Solders of the 15-85 Tin-lead Type

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(Cleveland Meeting, October 1944)

In recent years, solders containing 20 per cent tin with no bismuth or cadmium have been developed by a few companies, and personnel have been properly instructed in their use. In addition, since the tin shortage, a number of solders containing less than 10 per cent Sn, and some with no tin, are being used in special applications; however, a solder of this type has yet to be developed that is satisfactory for general use.

Table 1.—*Composition Ranges Prescribed for a Commercial Substitute Solder*

Element	Per Cent
Tin	18.0–20.0
Bismuth (maximum)[a]	0.80
Silver	0.10–1.25
Bismuth plus silver (minimum)	0.85
Antimony (maximum)	0.50
Copper (maximum)	0.13
Other elements, each (maximum)[b]	0.03
Lead	balance

[a] When silver is present in excess of 1 per cent, the Bi content shall be 0.50 per cent or over.
[b] Total not to exceed 0.10 per cent.

The purpose of this investigation was to develop an alloy containing a maximum of 15 per cent tin, with no cadmium or bismuth, having solder properties equivalent to or better than those of substitute solders now specified containing 18 to 20 per cent tin (Table 1), or even approaching the properties of the standard 40 to 60 tin-lead solder. The wartime restriction of bismuth and cadmium, elements that have beneficial effects on fluidity, solidification range and strength, makes it increasingly difficult to develop a general-purpose solder containing a maximum of 15 per cent tin.

In the course of this investigation, 11 elements were used in various combinations with the basic 15-85 tin-lead alloy. These elements were antimony, silver, copper, indium, thallium, lithium, calcium, barium, potassium, sodium and arsenic. In all, 116 low-tin solders were investigated, with the idea of developing a solder that will give satisfactory working properties, specifically in regard to "wetting" of copper, brass and iron, solidification range, capillarity and shear strength of a soldered joint. The relative importance of these various properties plays an important role in the search for substitute solders, since it is almost impossible to retain all of the desired qualities of a high-tin solder and still make drastic changes in the alloy composition. Because of the expected uses of a general-purpose solder, it is necessary that it have properties, especially in regard to wettability, that will enable it to be used on the metals in common use.

BASIC CONSIDERATIONS

The maximum liquidus temperature of a solder is determined by the particular application involved and the temperature that can be obtained by the source of heat. If a soldering iron is used, it must not only

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melt the solder but also heat to the soldering temperature the components being soldered. High temperature may cause excessive oxidation of the solder and also may injure the components of a soldered joint by buckling, warping, and so forth. This is very important in connection with fine radio equipment. When a torch or furnace is used to heat the parts of a soldered joint, high temperature may bring about an undesirable change in the physical properties of the components, either by a change in metallurgical structure or by excessive penetration of the solder.

The solidification range is of utmost importance in governing the "workability" of a solder. If the range is too great, the segregation of intermetallic compounds causes sluggishness before complete solidification. Excessive thickness of the intermetallic compound layers causes a decrease of joint strength. Also, it may be difficult to hold the components rigid during the solidification of the solder. On the other hand, if the temperature range is too narrow, the solder will solidify before sufficient spreading and penetration has taken place. The solidification range of a general-purpose solder must be a compromise between the two extremes.

The "wetting" quality of a solder, or its ability to spread on the base metal, is a property that, along with the liquidus temperature, largely determines the ease of the soldering operation. The mechanism of wetting is essentially one of surface tension, which in turn is dependent upon the difference between the cohesive forces within the solder itself and the adhesive forces between the solder and the base metal. In order to have good wetting, the adhesive forces must greatly exceed the cohesive forces.[2]

The forces involved in capillarity are similar to those in wetting of a flat surface, except that in the former adhesion is acting against gravity. In addition, the distance between the components being soldered plays an important role, as capillary action varies inversely with the distance. Experimental work by other investigators has shown that the soundest soldered joints are obtained with clearances of from 0.003 to 0.005 in., which indicates the importance of the wetting and capillary qualities of the solder, since these two properties are responsible for penetration into such small openings.

The tensile strength of solder itself bears little relation to the strength of a soldered joint. The important factors are the thickness of the solder layer and the nature of the bond between the solder and the components. Dirt, oxides, flux and excess intermetallic compounds all tend to break the continuity of the solder bond and lessen the shear strength of a joint. The initial composition of the solder and base metal, the temperature and time of application, the lapse of time before testing, as well as the thickness of the solder layer, have a marked effect on the ultimate strength of a soldered joint. Since these factors also govern the formation of new phases (solid solutions or compounds) by the process of diffusion, it is evident that the effects of diffusion cannot be disregarded when considering all the factors that determine the strength of a soldered joint. However, owing to the time and effort involved, direct measurements on the actual effects of diffusion products on joint-shear or tear strength were not made in this investigation. A number of investigators[3,4,9] have treated the problem quite thoroughly.

The appearance of a solder, such as "bright and shiny" as compared with "dull or dark gray," may not mean a serious change of physical properties, but poor appearance may have a rather important effect on the mechanic who is accustomed to working with higher tin alloys, in that too much emphasis might be placed on the correlation between brightness and solderability. A comparison of the appearance as cast and after a period of storing offers a fairly good criterion on which to predict the amount of oxidation to be expected during storage.

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[2] References are at the end of the paper.

Experimental Procedures

The lead, tin and antimony used were of commercial purity, containing on the order of 0.1, 0 to 0.15 per cent total impurities. All other elements were of high chemical purity.

All alloys were made with 400-gram charges melted in 250-c.c. graphite crucibles, charcoal being used as a protective covering. Melting was done in an automatically controlled electric furnace. For ease of melting, master alloys with lead were used for silver and copper additions.

All melts were cast in a mold made from ½-in. angle iron. Care was taken to cast the charges so that each sample had a cross-sectional area of approximately 0.07 sq. in., to ensure a reasonably good comparison in the hand bend tests. A solder bar was taken to be "very ductile" if it could withstand a 180° bend without cracking; "ductile" if able to take a 180° bend with slight cracking; "slightly ductile" if the specimen fractured between 90° and 180°; "brittle" if the fracture occurred between 45° and 90°; and "very brittle" if the specimen fractured with an angle of less than 45°.

The appearance of the tops and bottoms of the alloy bars was noted shortly after casting and is given in the tables in self-explanatory terms. Observations were repeated after 4 months and are also recorded.

To ensure representative samples for chemical analysis, each cast bar of solder was broken into segments and filings were taken from the ends of each piece.

Thermal arrests were determined for all alloys. For each one a representative sample of approximately 70 grams, contained in a 1¾-in. nickel crucible, was melted in a controlled electric furnace. The charges were covered with fine charcoal, to prevent oxidation. To ensure reasonably slow cooling, the heated crucibles were placed in asbestos fiber packed in a 1000-c.c. beaker. A 30-gauge iron-constantan thermocouple was inserted well into the melt and millivolt readings were taken every 15 sec. Cooling rates through the critical ranges varied from 14° to 18°C. per minute. Because of the comparatively rapid cooling rates used in determining the thermal arrests, the temperatures obtained are reproducible only within ±2°C.

The "spread of a drop" test was used as a measure of wettability of a solder on base metal. Spreading tests on copper were made with all alloys and the results of most of these tests are expressed graphically on Figs. 6 to 9. Wetting tests were run on brass and iron also, with a selected group of solders from each of the composition series, the purpose being to determine the comparative wettability of the various solders on the three base metals.

Spread tests were made on plates that were ⅛ in. thick and were heated over a flat furnace element with the energy input controlled by a 110–220-volt autotransformer. To assure accurate measurement of the temperature, an iron-constantan thermocouple was peened to the upper surface of each plate. All wetting tests were of 15-sec. duration and were made at 60°C. above the liquidus of the alloy being tested. The eutectic flux, containing by weight 71 parts water, 19 parts $ZnCl_2$ and 10 parts NH_4Cl, was used to clean the surface of the plates—in addition to the flux, a weak acid was found to be necessary to clean iron.

The solder pellets used in the spreading tests were of constant volume (0.025 c.c.). Reproducibility of results was very good; variances in area of spread using the same solder were on the order of 0.00 to 0.02

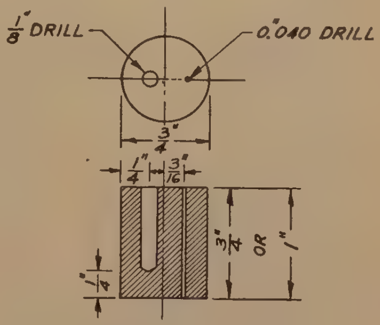
sq. in. Values reported are the average of four to six determinations.

The relative capillarity of the solders was determined by measuring the rise of an alloy column in a hole of 0.04-in. diameter, drilled in copper. The standard specimens were ¾-in. diameter and of various heights (Fig. 1).

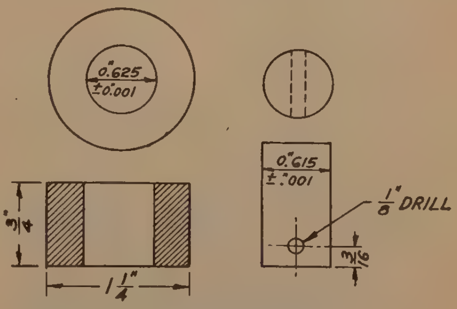
Specimens were heated in a pot resistance furnace. After fluxing, solder was applied for 15 sec. to the bottom of each vertically held specimen at a temperature of 60°C. above the liquidus of the solder. Since it was necessary to remove each specimen from the resistance furnace before fluxing and applying the solder, a brass ring was fastened to the specimen to decrease the cooling rate. The temperature was determined by means of a thermocouple, enclosed in refractory tubing, which was inserted in a hole drilled part way through the specimen.

For accurate determination of capillary rise, the specimens were radiographed by means of X-rays and measurements were made on the negative, using dividers and a steel rule calibrated to ⅟₁₀₀ in. The lead-base alloys show up sharply on the negative when placed on a viewing screen. The use of radiographs facilitated the measurements and showed any discontinuity present in the capillary column. The values reported are the average of two to four determinations. Reproducibility in this case is within ±0.05 inch.

To determine the shear strength of a soldered joint, the brass ring-and-plug type of specimen (Fig. 1) was used. A jig made of Transite board held the specimen together during heating and application of the solder. Each setup was heated in a pot resistance furnace to a temperature 60°C. above the liquidus of the solder. Both pieces were thoroughly fluxed with $ZnCl_2$-NH_4Cl mix. The solder was applied while the specimen was within the furnace and the ring was rotated to ensure the best tinning possible. Temperature control was obtained by means of a thermocouple peened to the specimen. When cool, excess solder was machined from the specimen and care was taken to make the top of the plug and the bottom of the specimen parallel, so that the direction of the compressive force of the tensile machine was along the axis, ensuring a positive shearing action. The rate of loading was kept nearly constant, the speed of the moving crosshead changing from about 0.04 to 0.02 in. per min. through the breaking range.



CAPILLARITY SPECIMEN



SHEAR TEST SPECIMEN

FIG. 1.—STANDARD SPECIMENS.

The highest shear strength was recorded, and this value was duplicated within 8 per cent in all cases, while the majority checked within 5 per cent or less. From two to five specimens were made with each alloy. The soundness of the joint was judged from the best shear strength ob-

TABLE 2.—*Comparison of the Properties of Substitute Solders*

PART 1

Alloy No.	Composition,[a] Per Cent	Thermal Arrests, Deg C.	Solidification Range, ΔT°C.
1	15 Sn, 85 Pb (basic alloy)	284–180	104
2[b]	19.1 Sn, 0.46 Sb, 0.87 Ag, 0.64 Bi, 0.06 Cu	270–178	92
3[c]	18.1 Sn, 0.52 Sb, 0.47 Ag, 0.60 Bi, 0.06 Cu	264–173	91
4	14.4 Sn, 0.96 Ag	283–178	104
5	14.1 Sn, 3.03 Ag	(317)–278–177	(140)–101
6	13.2 Sn, 5.08 Ag	(359)–280–176	(183)–104
7	14.1 Sn, 0.11 Cu	288–181	107
8	14.2 Sn, 0.20 Cu	288–182	106
9	40.0 Sn, 60.0 Pb	238–183	55
10	15.1 Sn, 0.06 Tl	284–181	103
11	14.2 Sn, 0.52 Tl	287–182	105
12	14.5 Sn, 0.68 Tl	285–179	106
13	14.2 Sn, 1.82 Tl	286–181	105
14	14.3 Sn, 0.50 Na	282–213–178	104
15	14.6 Sn, 0.24 Na	282–177	105
16	15.4 Sn, 0.03 Ca	286–180	106
17	15.4 Sn, 0.07 Ca	283–181	102
18	15.8 Sn, 0.10 Ca	283–180	103
19	14.6 Sn, 0.10 Ca	284–180	104
20	14.2 Sn, 2.00 Ag, 0.10 Cu	279–176	103
21	14.0 Sn, 2.03 Ag, 0.37 Cu	276–177	99
22	15.2 Sn, 1.00 In	279–173	106
23	15.3 Sn, 0.03 Li	282–176	106
24	15.4 Sn, 0.08 Li	286–179	107
25	15.4 Sn, 0.17 Li	282–178	104
26	15.3 Sn, 0.06 K	285–180	105
27	15.0 Sn, 0.10 K	288–184	104
28	15.0 Sn, 0.08 Ba	284–179	105
29	15.1 Sn, 0.75 Ba	285–182	103
30	14.3 Sn, 2.02 Ag, 0.75 In	271–169	102
31	14.3 Sn, 2.06 Ag, 1.30 In	270–167	103
32	13.1 Sn, 2.01 Ag, 0.90 In, 0.22 Cu	289–185	104
33	13.9 Sn, 2.00 Ag, 1.95 In, 0.21 Cu	271–159	112
34	14.3 Sn, 1.70 Sb	276–212–184	92
35	14.6 Sn, 2.56 Sb, 2.07 Ag	265–209–179	86
36	15.3 Sn, 2.24 Sb, 2.03 Ag, 0.07 Cu	266–212–180	86
37	14.9 Sn, 2.13 Sb, 2.04 Ag, 0.14 Cu	270–211–180	90
38	15.0 Sn, 2.13 Sb, 2.00 Ag, 0.06 Cu, 0.10 Na	268–180	88
39	15.0 Sn, 3.60 Sb, 1.93 Ag	258–225–180	78
40	14.74 Sn, 2.06 Ag, 0.25 In	275–172	103
41	14.82 Sn, 2.02 Ag, 0.54 In	267–168	99
42	14.50 Sn, 2.05 Ag, 0.34 In, 0.18 Cu	270–168	102
43	15.24 Sn, 1.50 Sb, 0.58 In	270–176	94
44	14.95 Sn, 2.06 Ag, 1.89 Sb	265–178	87
45	15.15 Sn, 1.26 Ag, 1.51 Sb	268–179	89
46	15.12 Sn, 1.03 Ag, 1.02 Sb, 0.66 Tl	267–188–180	87
47	14.48 Sn, 2.04 Ag, 0.72 Tl	275–175	100
48	15.24 Sn, 1.02 Ag, 0.94 Sb	270–179	91
49	15.10 Sn, 2.04 Ag, 0.96 Sb	268–177	91

PART 2

Alloy No.	Wetting, Sq. In.			Cap. Rise, In.	Shear Strength, Lb. per Sq. In.	Tinning[d] Property	Appearance after Casting	Appearance after Four Months	Bend Test[e]
	Cu	Brass	Fe						
1	0.14	0.185		0.49	4,280	F.	Shiny silver	Dull silver	V.D.
2	0.24	0.155	0.49	0.57	3,870	G.	Dull silver	Unchanged	V.D.
3	0.19	0.13	0.40	0.54	3,400	G.	Dull silver, scum on top	Unchanged	V.D.
4	0.15	0.11		0.32	4,040	G.	Slightly dull silver	Unchanged	V.D.
5	0.20	0.135	0.21	0.51	3,900	G.	Shrinkage porosity on top. Bright and etched on bottom	Unchanged	V.D.
6	0.20			0.505		G. (S. lumpy)	Appeared etched on top. Bright on bottom	Unchanged	V.D.
7	0.175	0.06		0.46	3,550	V.G.	Slightly dull silver	Unchanged	V.D.
8	0.195	0.08		0.47	4,130	V.G.	Slightly dull silver	Unchanged	V.D.
9	0.23	0.185		0.61	4,900	V.G.	Shiny silver	Unchanged	V.D.

[a] Balance lead. [b] High substitute. [c] Low substitute. [d] F., fair; G., good; V.G., very good.
[e] D., ductile; V.D., very ductile; S.B., slightly brittle; V.B., very brittle.

TABLE 2.—(*Continued*)

Alloy No.	Wetting, Sq. In.			Cap. Rise, In.	Shear Strength, Lb. per Sq. In.	Tinning[d] Property	Appearance after Casting	Appearance after Four Months	Bend Test[e]
	Cu	Brass	Fe						
10	0.14	0.13	0.37	0.49	3,420	V.G.	Slightly dull silver	Unchanged	V.D.
11	0.15	0.135	0.40	0.47	3,400	V.G.	Slightly dull silver	Slightly dull gray	V.D.
12	0.13			0.39	2,610	V.G.	Silvery	Unchanged	V.D.
13	0.135	0.15	0.32	0.51	3,680	V.G.	Slightly dull silver	Light gray	V.D.
14	0.18	0.23		0.56	2,360	G.	Dull gray scum	Unchanged	V.B.
15	0.14	0.105	0.36	0.48	3,970	G.	Dull silver	Grayish	V.D.
16	0.155	0.105	0.37	0.51	2,780	G.	Silvery	Silvery gray	V.D.
17	0.17			0.35	2,510	G.	Silvery	Light gray	D.
18	0.155	0.115	0.39	0.39	2,290	V.G.	Silvery	Dull gray	V.D.
19	0.15	0.14	0.37	0.45	2,720	G.	Dull silver	Grayish	S.B.
20	0.21	0.155	0.38	0.575	3,760	V.G.	Slightly dull silver	S. dull silver	D.
21	0.20	0.13	0.37	0.53	3,800	G.	Dull silver	Unchanged	S.B.
22	0.13	0.08	0.31	0.37	2,620	G.	Silvery	S. discolored	V.D.
23	0.135	0.155	0.41	0.40	2,710	G.	Dull silver	Unchanged	D.
24	0.15	0.125	0.41	0.39	2,760	G. (oxide grit)	Dull silver	Light gray	S.B.
25	0.15			0.40	2,240	F. (scummy)	Light gray	Darker gray	S.B.
26	0.15			0.39	2,960	G.	Dull silver, scum on top	Light gray	S.B.
27	0.15	0.15	0.42	0.41	2,290	G.	Dull scum on top; dull silver	Dull gray	S.B.
28	0.17	0.145	0.41	0.37	3,690	G.	Dull silver, black oxide	Silvery gray	D.
29	0.15	0.10	0.37	0.48	2,790	F. (oxide grit)	Scummy, porous; dull silver	Light gray	V.D.
30	0.28			0.46	3,430	G. (S. lumpy)	Dull scum, dull silver	Unchanged	D.
31	0.29	0.12	0.30	0.49	3,620	G. (S. lumpy)	Dull scum, dull silver	Unchanged	D.
32	0.16			0.485	4,400	G.	Silvery	Dull silver	V.D.
33	0.17	0.16	0.38	0.47	3,470	G.	Silvery	Dull silver	V.D.
34	0.10	0.07		0.37	4,190	F.	Smooth, bright silver	S. dull silver	V.D.
35	0.16	0.10	0.25	0.50	4,300	V.G.	Slightly dull silver	Unchanged	D.
36	0.13	0.06	0.33	0.47	4,220	V.G.	Dull silver	Unchanged	V.D.
37	0.11	0.08	0.28	0.49	4,120	V.G.	Dull silver	Unchanged	S.B.
38	0.13	0.075	0.32	0.48	3,530	F., oxide grit	Dull silver	Light gray	S.B.
39	0.12	0.095		0.53	3,870	V.G.	Slightly dull	Unchanged	D.
40	0.20			0.51	3,440	G.	Bluish scum, dull silver (scum disappeared on remelting)	Unchanged	D.
41	0.28			0.46	3,620	G.	Bluish scum, dull silver (scum disappeared on remelting)	Unchanged	D.
42	0.30			0.49	3,710	G.	Bluish scum, dull silver (scum disappeared on remelting)	Unchanged	D.
43	0.11			0.37	3,210	G.	Bluish scum, dull silver (scum disappeared on remelting)	Unchanged	D.
44	0.15			0.45	3,980	G.	Dull silver (some scum)	Unchanged	D.
45	0.16			0.48	3,720	G.	Dull silver (some scum)	Unchanged	D.
46	0.145				3,660	F.	Dull silver	Unchanged	D.
47	0.15			0.46	4,080	G.	Dull silver (some scum)	Unchanged	D.
48	0.16			0.49	3,620	G.	Dull silver (some scum)	Unchanged	D.
49	0.22			0.47	3,830	G.	Dull silver (some scum)	Unchanged	D.

tained and the appearance of the bond after testing.

Tinning qualities were determined mainly by the readiness with which the solder adhered to a clean iron. A solder was said to have good tinning quality if it wet the iron readily. It is important in this respect that the solder be retained in a reasonably large globule, without excessive scum formation. In addition, as a further test for workability, copper wire was soldered to copper terminal lugs and to copper plate. Rosin flux was used for this. The soldering iron was filed and cleaned with eutectic zinc-ammonium chloride flux before each solder was tested.

The various tests just described are believed by the authors to be adequate for determining the basic properties of the general-purpose solder with which this work is concerned. Other investigators have used different types of quantitative tests to study the properties covered in this paper, and it is realized that other properties are of equal or greater importance under certain conditions of stress and temperature.

The results of the tests are listed in Table 2 and are shown graphically on Figs. 2 to 11. All the alloys investigated are not reported in this table but the figures offer a ready interpretation of the data on 116 alloys. It was not the intent of this work to investigate thoroughly the effects of any one element or group of elements on the basic alloy formed of 15 per cent Sn, balance Pb. Consequently, additional data obtained from further investigation may result in modification of some of the curves on Figs. 2 to 11.

In this investigation the effect of antimony on the solidification range and "wetting" was found to be of much greater magnitude than that of any other element. Eight per cent antimony added to an alloy of 15 per cent Sn, balance Pb, will reproduce almost exactly the solidification range of 40-60 tin-lead solder (liquidus 238°C., solidus 183°C.). No other element or group of elements was found to be very effective in reducing the liquidus temperature of the 15 per cent Sn alloy. For this reason, it was believed desirable to approach the problem by studying mainly the effects of alloy additions on the 15 per cent Sn, balance Pb and the 15 per cent Sn, plus Sb, balance Pb systems.

The lowest temperature given in each case under "thermal arrests" (Table 2) does not represent a true solidus, because the melts were not cooled under equilibrium conditions (not stirred) and consequently segregation of lead-tin and tin-antimony compounds occurred. The segregation of the lead-tin compound causes a separation of the eutectic or nearly eutectic lead-tin melt, which accounts for the large number of low arrests at approximately 180°C. The separation of the low-melting constituent was found not to affect the strength of a soldered joint; that is, the temperature of the lowest arrest in each case was not significant as far as the softening point of the solder in a joint was concerned. Tests have shown that the softening temperature closely approaches the actual solidus of the Pb-Sn and Pb-Sn-Sb systems (at 15 per cent Sn), whichever the case may be.

Silver lowers the liquidus temperature of the basic alloy and is useful in this respect. However, when silver is present in amounts over 2 per cent, an excess of the compound Ag_3Sn forms, which has a high melting point. The Ag_3Sn compound is undesirable in general-purpose solders, because at ordinary soldering temperatures the compound causes the solder to become sluggish.

The effect of antimony and 2 per cent silver plus antimony on the solidification range of the base alloy is shown on Fig. 2.

The properties of a substitute solder (No. 3, Table 2) with a composition falling within the ranges prescribed for a commercial solder (Table 1), were used as a basis for determining an acceptable solder in this investigation. In Table 3 these properties are compared with those of four other solders. Property requirements were based on experimental procedures described in this report. Owing to the nature of the test, small variances were considered allowable in capillary rise. A solder was not disqualified if the solidification range was 10° to 12°C. above that of the reference solder, as the slight increase does not impair the workability provided that personnel are instructed properly in the use of such solders.

As a single addition element, silver proved most beneficial to the basic 15-85 tin-lead alloy; however, the effects of silver were improved by further alloy additions. For example, the 2 per cent Ag, low-indium, low-copper combination gave satisfactory joint shear strength (Fig. 10) and excellent spreading (Fig. 9), the latter even surpassing that of the 18 to 20 per cent

TABLE 3.—*Comparison of Two Substitutes Developed in This Investigation with Those of the Basic 15-85 Tin-lead Alloy and Two Commercial Solders*

Data	Commercial Solders[a]		In This Investigation		Basic Alloy No. 1
	Substitute Solder No. 3	40-60 Tin-lead No. 9	Best Substitute Solder No. 42	2nd Best Substitute Solder No. 49	
Solidification range (ΔT°C.)	91	55	102	91	104
Wetting on copper, sq. in.	0.19	0.23	0.30	0.22	0.14
Joint shear strength, lb. per sq. in.	3,400	4,900	3,710	3,830	4,280
Capillary rise, in.	0.54	0.61	0.49	0.47	0.49
Tinning properties	Good	V. good	Good	Good	Fair
Ductility	Good	V. good	Good	Good	Good
Composition, per cent:					
Sn	18.10	40.00	14.50	15.10	15.0
Ag	0.47		2.05	2.04	
In			0.34		
Cu	0.06		0.18		
Sb	0.52			0.96	
Bi	0.60				
Pb	Balance	Balance	Balance	Balance	Balance

[a] Numbers refer to Alloy No. on Table 2.

tin reference solder and the commercial 40-60 tin-lead solder.

Summary of Effect of Alloying Additions on Properties of the 15-85 Tin lead Base Alloy as Determined in This Investigation

Antimony.—Decreases liquidus and solidification range; has a deleterious effect on wettability on copper (this holds true in the presence of silver but to a lesser extent); increases joint shear strength when present in amounts over 2 per cent (in the presence of silver, less antimony is required to produce this effect); decreases capillary rise, but increases it in the presence of silver; does not impair ductility in amounts less than 4 per cent; improves appearance of the base alloy.

Silver.—Lowers the major liquidus in amounts up to approximately 4 per cent Ag, but sharply increases the complete liquidus temperature when present in amounts over 2 per cent, because of the formation of Ag_3Sn; increases the wettability considerably; up to 2 per cent improves the general effect of *low* antimony on the base alloy; raises further the solidification range, but improves slightly the wettability of the base alloy containing high antimony (+4 per cent); improves appearance and ductility; improves capillary action with or without antimony; lowers joint shear strength but raises it when present with 1.5 to 2.5 per cent Sb.

Indium.—In amounts up to 1 per cent has no appreciable effect on wettability; lowers both liquidus and solidus considerably; greatly increases wettability in the presence of silver; impairs capillary action and joint shear strength except in the presence of silver; with additions over 1 per cent increases solidification range (mainly by lowering solidus temperature) in the presence of silver and copper, and decreases wettability under similar circumstances; improves the appearance and ductility; in amounts up to 1 per cent increases considerably the joint shear strength of the silver-copper combination; is beneficial in lead-silver solders.

Copper.—Slightly increases the solidification range with additions up to 0.2 per cent; improves the wettability considerably; has no great effect on joint shear strength; impairs further the effect of antimony on wettability; does not improve the properties of the antimony-silver system; is desirable in amounts up to 0.25

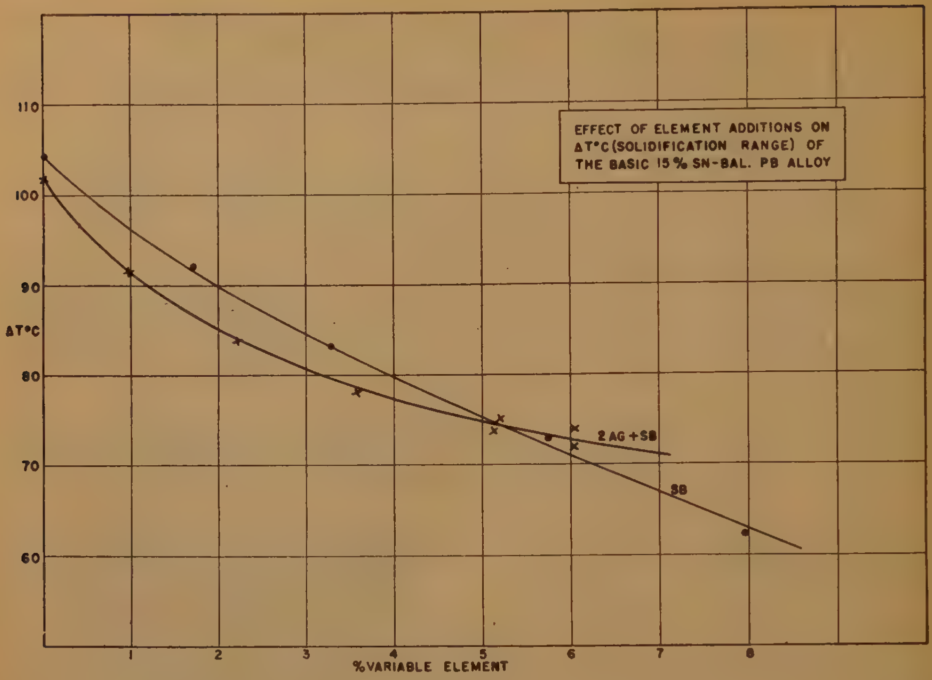

EFFECT OF ELEMENT ADDITIONS ON
ΔT°C (SOLIDIFICATION RANGE) OF
THE BASIC 15% SN-BAL. PB ALLOY
110
100
90
ΔT°C
80
70
60
2 AG + SB
SB
1
2
3
4
5
6
7
8
% VARIABLE ELEMENT

FIG. 2.

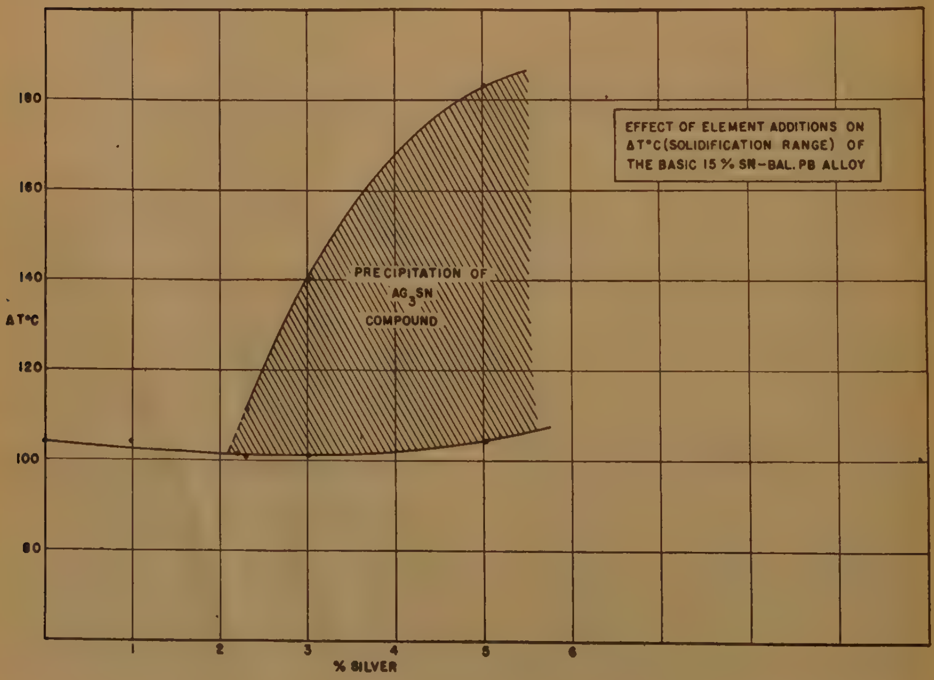

EFFECT OF ELEMENT ADDITIONS ON
ΔT°C (SOLIDIFICATION RANGE) OF
THE BASIC 15% SN-BAL. PB ALLOY
PRECIPITATION OF
AG3SN
COMPOUND
180
160
140
ΔT°C
120
100
80
1
2
3
4
5
6
% SILVER

FIG. 3.

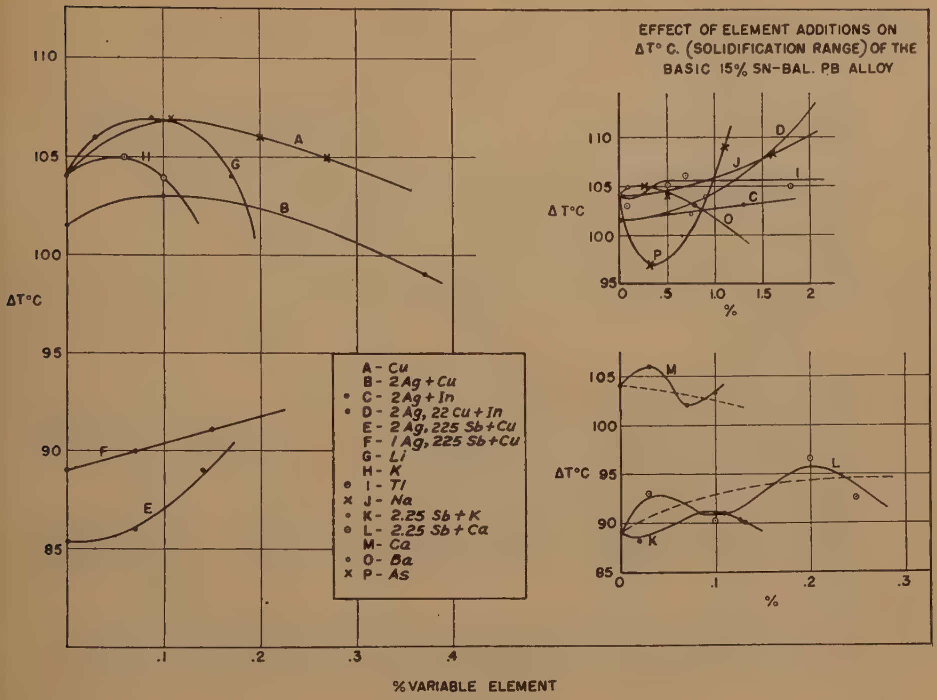

EFFECT OF ELEMENT ADDITIONS ON ΔT° C. (SOLIDIFICATION RANGE) OF THE BASIC 15% SN-BAL. PB ALLOY
110
105
100
95
90
85
ΔT°C
.1
.2
.3
.4
A
B
E
F
G
H
A - Cu
B - 2 Ag + Cu
• C - 2 Ag + In
• D - 2 Ag, 22 Cu + In
E - 2 Ag, 225 Sb + Cu
F - 1 Ag, 225 Sb + Cu
G - Li
H - K
I - Tl
× J - Na
K - 2.25 Sb + K
L - 2.25 Sb + Ca
M - Ca
O - Ba
× P - As
ΔT°C
0
.5
1.0
1.5
2
%
C
D
I
J
O
P
M
K
L
.1
.2
.3
%
% VARIABLE ELEMENT

FIG. 4.

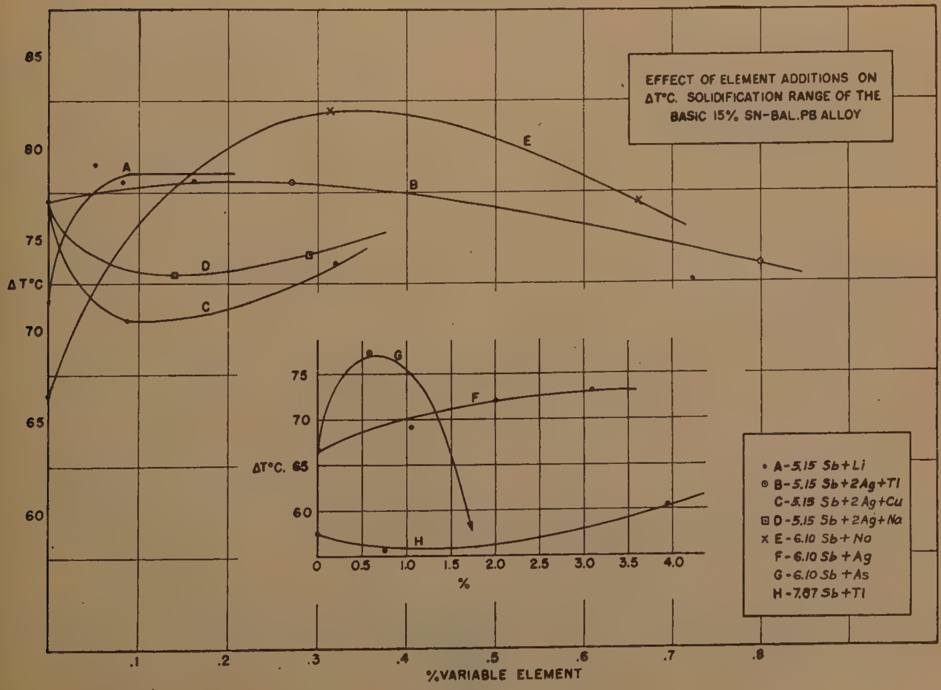

EFFECT OF ELEMENT ADDITIONS ON ΔT°C. SOLIDIFICATION RANGE OF THE BASIC 15% SN-BAL. PB ALLOY
85
80
75
70
65
60
ΔT°C
A
B
C
D
E
F
G
H
75
70
ΔT°C. 65
60
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
%
• A - 5.15 Sb + Li
B - 5.15 Sb + 2 Ag + Tl
C - 5.15 Sb + 2 Ag + Cu
D - 5.15 Sb + 2 Ag + Na
× E - 6.10 Sb + Na
F - 6.10 Sb + Ag
G - 6.10 Sb + As
H - 7.87 Sb + Tl
.1
.2
.3
.4
.5
.6
.7
.8
% VARIABLE ELEMENT

FIG. 5.

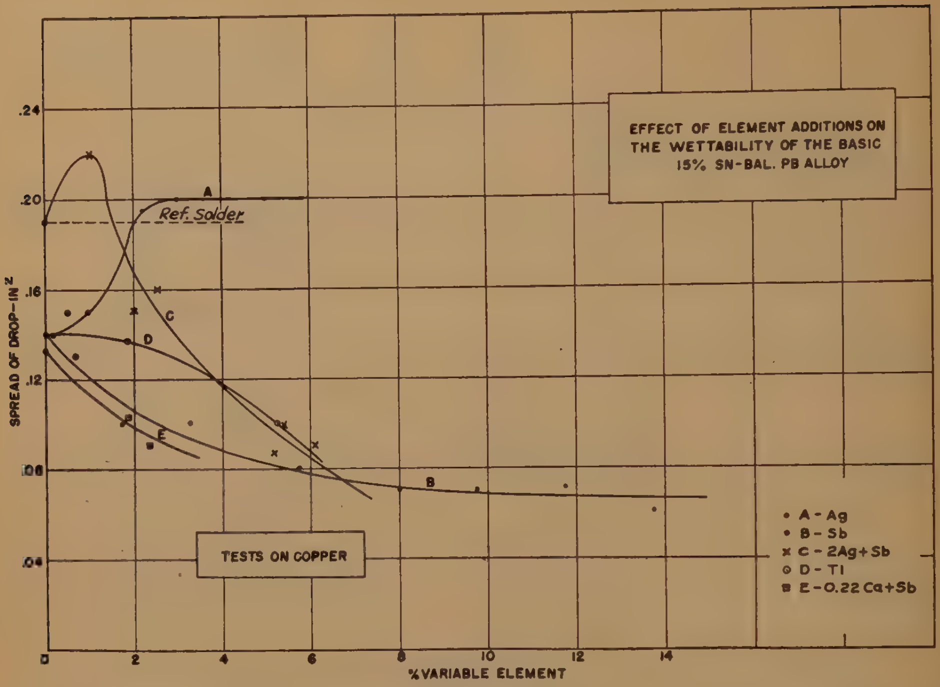

.24
.20
.16
.12
.08
.04
0
2
4
6
8
10
12
14
SPREAD OF DROP–IN²
%VARIABLE ELEMENT
EFFECT OF ELEMENT ADDITIONS ON
THE WETTABILITY OF THE BASIC
15% SN-BAL. PB ALLOY
Ref. Solder
A
B
C
D
E
TESTS ON COPPER
• A - Ag
• B - Sb
× C - 2Ag+Sb
○ D - Tl
■ E - 0.22 Ca+Sb

FIG. 6.

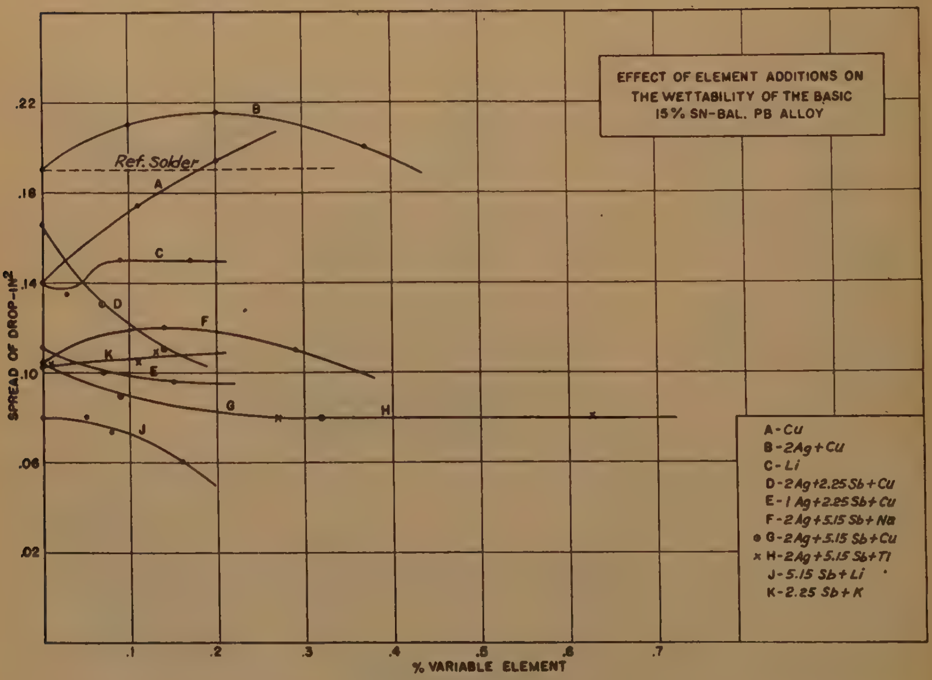

.22
.18
.14
.10
.06
.02
.1
.2
.3
.4
.5
.6
.7
SPREAD OF DROP–IN²
% VARIABLE ELEMENT
EFFECT OF ELEMENT ADDITIONS ON
THE WETTABILITY OF THE BASIC
15% SN-BAL. PB ALLOY
Ref. Solder
A
B
C
D
E
F
G
H
J
K
A - Cu
B - 2Ag+Cu
C - Li
D - 2Ag+2.25 Sb+Cu
E - 1 Ag+2.25 Sb+Cu
F - 2Ag+5.15 Sb+Na
● G - 2Ag+5.15 Sb+Cu
× H - 2Ag+5.15 Sb+Tl
J - 5.15 Sb+Li
K - 2.25 Sb+K

FIG. 7.

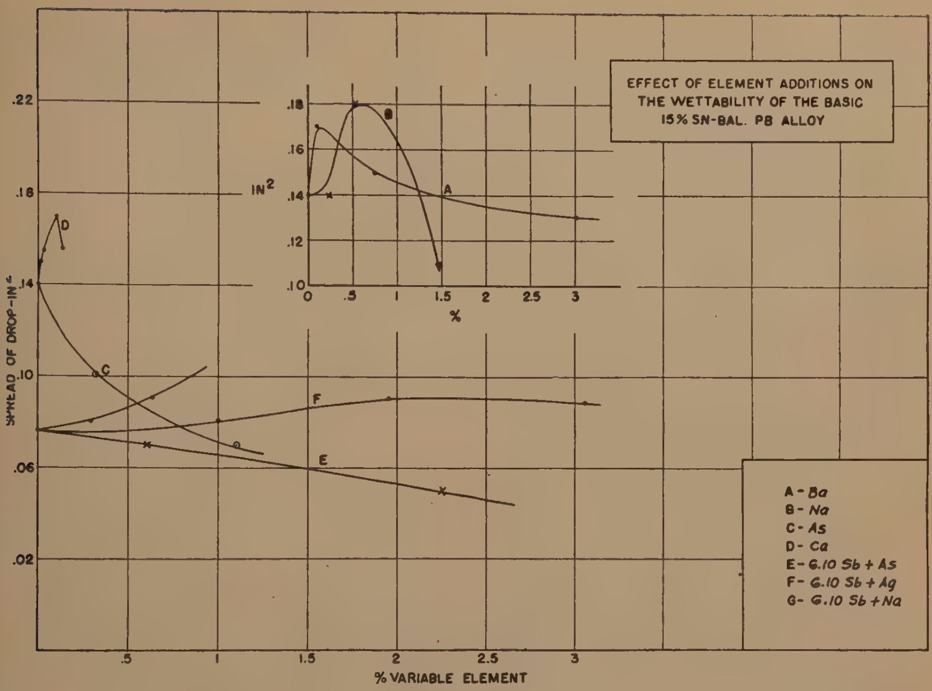

EFFECT OF ELEMENT ADDITIONS ON
THE WETTABILITY OF THE BASIC
15% SN-BAL. PB ALLOY
SPREAD OF DROP-IN²
.22
.18
.14
.10
.06
.02
.5
1
1.5
2
2.5
3
% VARIABLE ELEMENT
IN²
.18
.16
.14
.12
.10
0
.5
1
1.5
2
2.5
3
%
A
B
C
D
E
F
A - Ba
B - Na
C - As
D - Ca
E - G.10 Sb + As
F - G.10 Sb + Ag
G - G.10 Sb + Na

FIG. 8.

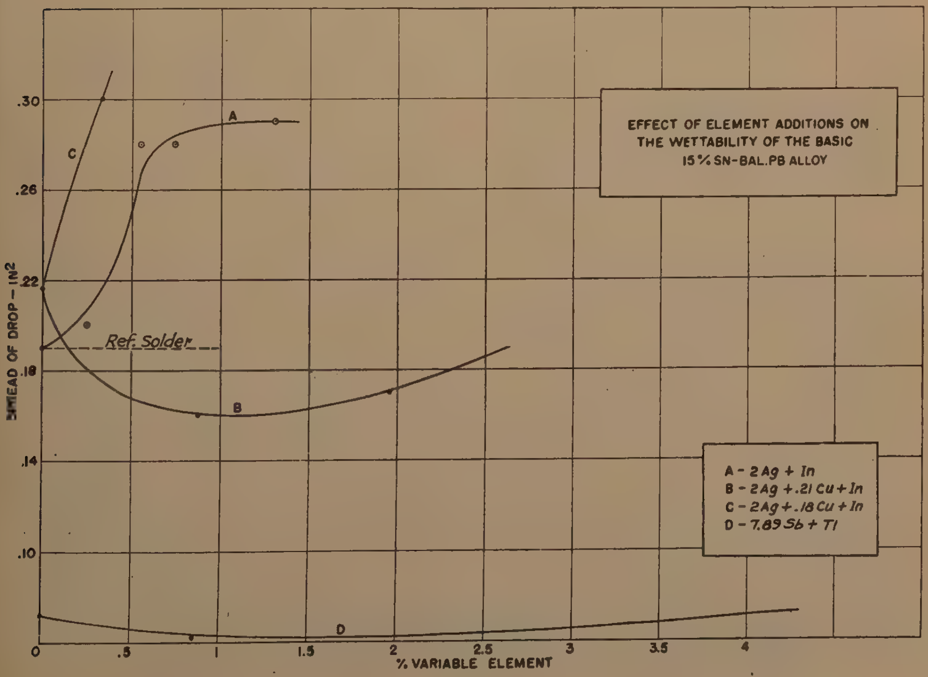

EFFECT OF ELEMENT ADDITIONS ON
THE WETTABILITY OF THE BASIC
15% SN-BAL.PB ALLOY
SPREAD OF DROP – IN²
.30
.26
.22
.18
.14
.10
0
.5
1
1.5
2
2.5
3
3.5
4
% VARIABLE ELEMENT
A
B
C
D
Ref. Solder
A - 2Ag + In
B - 2Ag + .21 Cu + In
C - 2Ag + .18 Cu + In
D - 7.89 Sb + Tl

FIG. 9.

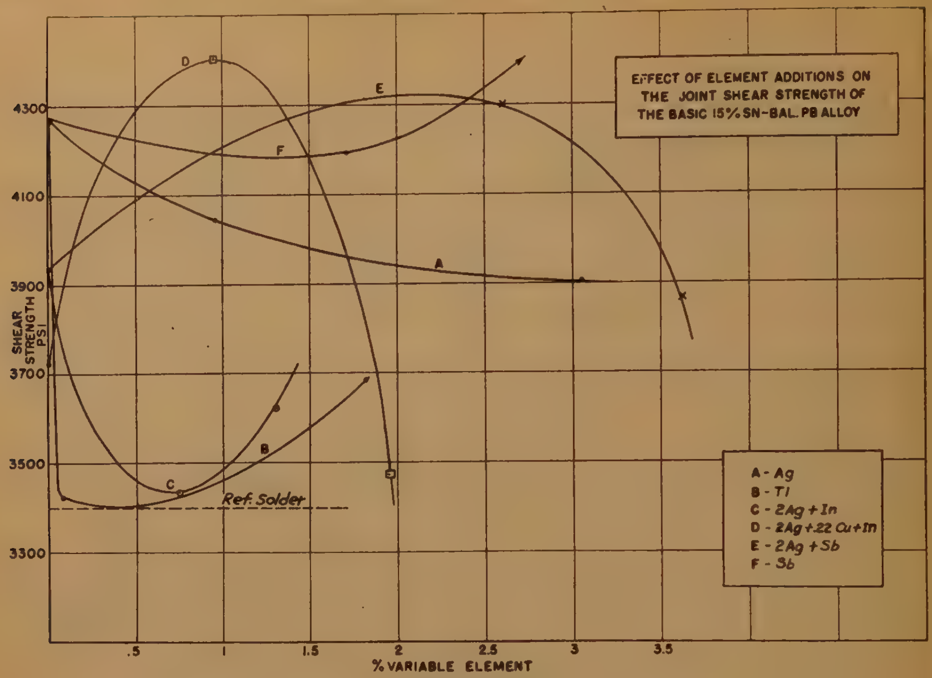

EFFECT OF ELEMENT ADDITIONS ON THE JOINT SHEAR STRENGTH OF THE BASIC 15% SN-BAL. PB ALLOY
SHEAR STRENGTH PSI
4300
4100
3900
3700
3500
3300
.5
1
1.5
2
2.5
3
3.5
% VARIABLE ELEMENT
A
B
C
D
E
F
Ref. Solder
A - Ag
B - Tl
C - 2Ag + In
D - 2Ag + .22 Cu + In
E - 2Ag + Sb
F - Sb

FIG. 10.

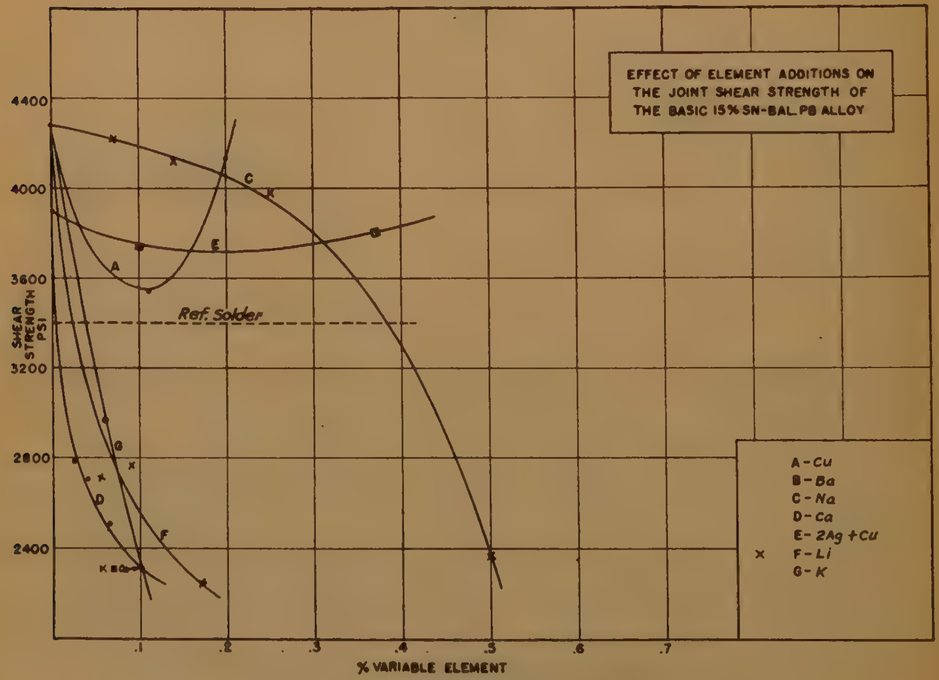

EFFECT OF ELEMENT ADDITIONS ON THE JOINT SHEAR STRENGTH OF THE BASIC 15% SN-BAL. PB ALLOY
SHEAR STRENGTH PSI
4400
4000
3600
3200
2800
2400
.1
.2
.3
.4
.5
.6
.7
% VARIABLE ELEMENT
A
C
D
E
F
G
K
B
Ref. Solder
A - Cu
B - Ba
C - Na
D - Ca
E - 2Ag + Cu
x F - Li
G - K

FIG. 11.

per cent with the silver-indium alloys provided that indium is less than 1 per cent; is desirable in small percentages with the silver addition.

Thallium.—Has little effect on solidification range; decreases wettability in quantities over 1.5 per cent; has no effect on capillary rise; decreases joint shear strength slightly; in general does not improve the properties of the high-antimony and antimony-silver solders; causes a slight tarnish with time; does not impair ductility; increases joint shear strength but otherwise does not enhance the effect of silver. Care should be taken in its use because of its toxic properties.

Sodium.—Up to 0.5 per cent has a negligible effect on the solidification range, but at the same time increases the wettability; cannot be used in quantities above 0.25 per cent because of its deleterious effect on ductility and appearance; tends to increase the fluidity; increases slightly the wettability of the antimony and antimony-silver additions; gives a surprisingly high joint shear strength; will cause slight brittleness in presence of antimony and copper but is not disqualifying in this respect. Sodium, however, is quite impractical in some applications with the other alkali metals, because of its reactivity. This is easily perceivable on any exposed molten puddles of alloys containing these metals.

Lithium.—Raises slightly the solidification range in amounts up to 0.1 per cent; greatly decreases joint shear strength by the presence of oxide grit; offers no improvement to the high-antimony addition; impairs the general workability of the alloy, mainly because of its high dross formation; can be disqualified as a possible addition element.

Potassium.—Has no appreciable effect on the solidification range or on wettability, with or without antimony; greatly decreases the joint shear strength; is detrimental to capillary qualities; is disqualified as an addition element; should not be allowed to exceed 0.02 to 0.03 per cent.

Calcium.—Has no appreciable effect on the solidification range with or without antimony; increases wettability in amounts not over 0.1 per cent; impairs capillarity; causes oxide grit, which is extremely detrimental to joint shear strength; is not beneficial as an addition element; should not exceed 0.02 to 0.03 per cent.

Barium.—Has a negligible effect on the solidification range in amounts up to 1 per cent; increases wettability in quantities up to approximately 0.2 per cent; is slightly detrimental to capillary rise; will not greatly decrease joint shear strength in quantities less than 0.15 per cent; causes high dross and oxide grit in amounts over approximately 0.2 per cent; may be considered a beneficial addition to the base alloy in amounts up to 0.15 per cent.

Arsenic.—Lowers considerably the solidification range of the base alloy in amounts up to 0.3 to 0.4 per cent, after which there is a sharp increase; decreases wettability in any amount; offers no beneficial effect in the presence of high antimony; over approximately 2 per cent promotes large grain size, which in turn decreases ductility; should not exceed 0.1 to 0.15 per cent in a 15 per cent Sn solder. Arsenic is poisonous and therefore should be used with discretion.

SUMMARY AND CONCLUSIONS

Of the alloys investigated, nine passed property requirements; i.e., Nos. 8, 20, 21, 30, 31, 40, 41, 42, 49, listed in Table 2. A second group of alloys, which closely approach the requirements, are Nos. 5, 6, 7, 11, 15, 32, 35 through 39, 44, 45, 47 and 48. Alloys 5, 6, 7, 11 and 15 can be used best where slightly higher temperatures can be obtained, as in torch soldering. The remainder of the alloys in the second group may be considered general low-grade solders and can be used in jointing, coating and in moderately high-temperature uses and dip soldering, where wettability is not too important.

TABLE 4.—*Recommended Composition Ranges for Substitute Solders of the* 15 *Per Cent Tin Class*

PER CENT

Solder	Tin	Silver	Indium	Antimony	Copper	Lead
1	14.5–15.5	1.7–2.0	0.3–0.5		0.15–0.25	Balance
2	14.5–15.5	1.6–2.0	0.5–1.0			Balance
3	14.5–15.5	1.7–2.0		0.8–1.2		Balance
4	14.5–15.5	1.7–2.0			0.1 –0.35	Balance
5	14.5–15.5				0.15–0.25	Balance

It is to be noted that only one solder containing antimony (No. 49) passed requirements (except in capillary rise). Only this alloy has a solidification range comparable with that of the reference solder (No. 3, Table 2) and at the same time has better wettability. Alloys 44, 45 and 48, containing 2 Ag and 2 Sb, 1.25 Ag and 1.50 Sb and 1 Ag and 1 Sb, respectively, closely approach but do not meet the wetting requirement. However, as was pointed out in the previous paragraph, these solders can be used in limited applications, especially those in which the components are easily accessible. Of the indium-bearing solders, Nos. 41 and 42 look most promising. The silver, low-indium, low-copper combination imparts very satisfactory properties to the base alloy.

To produce a 15 per cent Sn solder, containing neither cadmium nor bismuth and having solidification and wetting properties comparable with those of a high-tin solder, is only a remote possibility. The main reasons for this are:

1. Of the addition elements available, antimony is the only one that has an appreciable effect on the solidification range. No other element or group of elements was found to be very effective in reducing the liquidus temperature. However, in order to maintain satisfactory wettability, such as that required by a general-purpose solder, less than 1.2 per cent antimony must be used and this amount will not give a solidification range comparable with that of a higher tin solder.

2. The addition of silver, alone or with other elements, is limited to 2 per cent because of the formation of excess Ag_3Sn compound.

3. The use of indium is limited by its high cost, 1 per cent being the maximum amount economically feasible.

4. Of the remaining addition elements investigated—copper, thallium, sodium, calcium, lithium, potassium, barium and arsenic—none was found to improve to a satisfactory extent the wettability of a 15 per cent Sn alloy containing antimony.

In the course of this investigation, 15 per cent Sn solders having a solidification range comparable with or slightly above that of an 18 to 20 per cent Sn substitute solder—all other properties being satisfactory—have been developed. The composition ranges of this group of solders, as ascertained from the experimental data, are given in Table 4. These solders, especially Nos. 1 to 3, were found to be very good substitutes for the 20 per cent Sn solder and adequate substitutes in some applications for the 40-60 tin-lead solder.

Inasmuch as most solders are made from secondary metals, the results of this investigation should prove helpful in determining the maximum allowable impurities. Many of the residual impurities present in secondary metals have been covered in this investigation, and their actual effects individually, and to a lesser extent collectively, on the physical properties of the 15-85 tin-lead base alloy have been determined. It is felt that the restrictions on allowable impurities in substitute solders may be relaxed considerably.

Acknowledgment

Grateful acknowledgment is made to C. E. Jackson and A. L. Christenson for their helpful suggestions in conducting the work and in preparation of the manuscript, and to the analytical chemistry section; also to the Navy Department for sponsoring the work and for permission to publish the results.

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DISCUSSION

(*Bruce W. Gonser presiding*)

A Member.—I was interested in that list of solders. Is there any reason for listing them in that order?

J. B. Russell.—No, they were not listed in that order for any particular reason. We followed through with a chronological order based on composition. The most satisfactory additions were the indium-copper-silver and the silver-antimony. The silver-antimony addition to a basic lead-tin alloy is most commonly used at the present time.

P. A. Beck.*—I wonder whether the author could give any explanation of the cause of the effect of silver. Silver itself does not seem to bond to steel and I wonder by what mechanism silver increased the wettability of these solders. Could it be by an effect on the surface tension of the molten alloy?

J. B. Russell.—The effect of silver on surface tension was the idea we had in mind.

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* Cleveland Graphite Bronze Co., Cleveland, Ohio.

I cannot think of any other reason, theoretical or otherwise, that would account for the increase in wettability. An increase in fluidity will accompany a decrease in surface tension. We note that in use of solders of this type on iron we always have a very fine film preceding the actual spread, which indicates a surface tension effect. This effect is not as pronounced on copper or brass which probably may be attributed to the greater tendency toward diffusion and the formation of intermetallic compounds.

H. E. MOSER.*—Would the author care to tell us whether he used any different methods in making the shear-test specimens. I think finally heat was applied and a flux simultaneously. Was any work done in which the flux and solder were applied first, and then the heat?

J. B. RUSSELL.—No, we did not do such work. Our specimen assembly was heated in the furnace and the solder was applied when the whole assembly was fully up to temperature. Flux was applied during the heating as well as when the specimen was at the soldering temperature.

H. E. MOSER.—What kind?

J. B. RUSSELL.—Eutectic zinc-ammonium-chloride.

B. W. GONSER.*—There are so many factors that influence an operation of this type—the kind of flux, the solder composition, temperature, etc., that it is hard to keep conditions constant so that the effect of only one factor at a time can be followed.

One item of particular interest in this paper is the effect of indium as a useful constituent in substitute solders. After the restrictions are removed how would you place indium? Do you think that it is merely replacing an equivalent amount of tin? Would tin have the same effect or a better effect than that amount of indium?

J. B. RUSSELL.—I believe that indium replaces more than an equivalent amount of tin when combined with silver, at least from a standpoint of increasing wettability. However, because of its high cost there would be no advantage in using the indium-silver in a peacetime economy if plenty of tin was available. It would be well to mention that the indium-silver combination might impart very desirable creep properties to a solder joint. An increase of tin does increase creep of a soldered joint, whereas the indium-silver combination may not be as pronounced in this respect. If this is substantiated by further investigation, it is quite possible that indium will be used in special purpose postwar solders requiring better creep strength at high temperatures and at the same time having comparatively low operating temperatures.

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* Battelle Memorial Institute, Columbus, Ohio.

SYMPOSIA

Symposium on Creep of Nonferrous Metals and Alloys

(Cleveland Meeting, October 1944)

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INTRODUCTION

THE Symposium on Creep of Nonferrous Metals and Alloys convened at 9.45 o'clock, in the Euclid Room, Hotel Statler, Cleveland, Ohio, on Tuesday, Oct. 17, 1944, H. L. Burghoff and E. E. Schumacher presiding.

The following pages contain the papers and discussions presented.

Application of Nonferrous Metals and Alloys in Stress Design

By J. J. Kanter,* Member A.I.M.E.

(Cleveland Meeting, October 1944)

The choice of a nonferrous metal or alloy for a given application is frequently predicated upon a consideration of properties other than merely the capacity to withstand stress. When ability to withstand stress is the dominant engineering requisite of the material to be used, economic considerations seldom lead to the choice of nonferrous metals and alloys. In most instances where a nonferrous metal is used it is because of some special quality of either corrosion resistance, electrical properties, thermal properties, antifriction, or fabrication advantage that commends its application. The mechanical properties, as a rule, present an incidental engineering consideration entirely secondary to the special quality deciding its use. Indeed, great ingenuity has often been exhibited by engineers and metallurgists in overcoming the mechanical shortcomings of a nonferrous base material, in order to take advantage of some outstanding property.

With this thought in mind, we might better appreciate some of the problems in stress design encountered with nonferrous metals and alloys pertinent to a symposium on their creep characteristics. Our considerations must necessarily be far from complete because of the broad range of materials in the nonferrous category for which creep properties assume a technical interest. Creep deformation of these metals can be subject for study at temperatures ranging from ambient to incandescent, depending upon which one is under consideration. Whereas the steel metallurgist thinks of creep as an essentially high-temperature engineering consideration, the same is not necessarily true in the field at hand.

The diversity of the creep problems in the nonferrous field is perhaps accountable to some extent for its virginity as a symposium subject. Each research has necessarily been sponsored by some organization or group interested either in promoting the use of a certain nonferrous base or in obtaining data toward the solution of a mechanical difficulty encountered in applying a material indispensable for its special attributes. Perhaps as many techniques of creep testing have been used as there are base metals implied under "nonferrous." Some of the creep problems that have occasioned researches are associated with steam-pressure vessels such as tubes, drums, castings, and forgings of copper-base and nickel-base alloys, cable sheathings of lead and lead-base alloys, electrical transmission lines of copper and aluminum, engine parts die-cast from alloys based on zinc, aluminum, copper—soldered and brazed joints—as well as numerous duties at extremely high temperatures met with alloys based on cobalt, nickel, tungsten, molybdenum, platinum, and other precious or semiprecious metals. Postwar technology will have the benefit of much creep research on nonferrous metals, which for reasons of security cannot be discussed on this occasion.

SUITABILITY OF METALS

As already intimated, the bulk of the constructional metal that ordinarily is

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associated with the term "nonferrous" is not eminently suited for applications involving high stress or high temperature when creep resistance is essential. This may sound like a too negative statement with which to introduce the present symposium, but in order to place a proper and practical engineering appraisal on the subject this circumstance must be faced. When pressure vessels made of copper-base alloys are used, either their ratings are abruptly limited to a comparatively mild elevation of temperature or else the copper-alloy part is devised to furnish protection over a ferrous reinforcing structure. A necessity for reinforcement is further exemplified by the steel cores used in electrical transmission lines. For high-duty application, soldering and brazing are supplanted by welding. Even in the field of heat-resisting alloys, the duty of resisting creep generally befalls the lot of ferrous-base materials, while the electrical duties, cladding of the ferrous material against the ravages of chemical activity, hard facing against abrasion and other special assignments become the role of the more precious nonferrous bases.

REPORTS OF RESEARCH

Although our present symposium is perhaps the first to specifically consider the creep of nonferrous metals and alloys, there have been previous efforts made to compile, review and present the published information in this field. Noteworthy is a research report of the British Non-Ferrous Metals Research Association in 1937, by W. H. Baker.[2] In 1938, the well-known volume on Compilation of Creep Data sponsored by the Joint A.S.T.M.-A.S.M.E. Committee on Effect of Temperature on the Properties of Metals,[3] contained a small section devoted to nonferrous metals. Since 1938 a number of further pertinent individual works on nonferrous creep have appeared, for which bibliography and abstract is appended to this paper. A goodly proportion of these later references are to be found in the Transactions of our Institute of Metals Division.

It is gratifying to note that the volume of reliable nonferrous creep data is growing. The need for information of this sort has perhaps been brought into focus through the A.S.M.E. Boiler Code Committee, which is responsible for the table of Maximum Allowable Working Stresses for Nonferrous Materials, to be found in the A.S.M.E. Code for Power Boilers. This tabulation of maximum stress values, listed for various metals temperatures and to be applied in the various mechanical design formulas established by the Code, covers various nonferrous materials, comprising copper-base, nickel-base and aluminum-base alloys. The values in the table have been arrived at by an appraisal of available tensile and creep data, as well as other pertinent properties.

In the March 1944 issue of *Mechanical Engineering*, on pages 210 and 211, appears a proposed extended revision of this table of nonferrous design stresses. It is to be hoped that the additional data brought forth by our symposium will prove useful to the Boiler Code Committee in authenticating some of the values needed for this table. A study of the table, and the realm of materials that it needs to cover, in contrast with available data, may serve to demonstrate that much further investigation and future symposiums on nonferrous creep are needed.

When stress design becomes codified, as it has in the aforementioned Boiler Code, the materials to which each value applies must be precisely specified and designated. This introduces the problems of defining in specifications each material in such a way as to guarantee the user the minimum creep-stress value anticipated in formulating the safe practices that it is the purpose of such a Code to enforce. How to frame specifications for creep resistance in materials has been something of a poser to those who have wrestled with this question for some years.

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[2] References are at the end of the paper.

While it is true that a creep investigation upon a material of some nominal designation delimits the creep behavior to be anticipated in the engineering use of that material, such behavior may still be far outside of satisfactory control. As has often been emphasized, in the literature on creep, this is a property exceedingly sensitive to slight structural differences, not controlled by the composition ranges, physical test ranges, and treatments possible under standard specifications for materials. Grain size, degree of cold-work, and minor impurities exert profound influences on the creep rates of metals. Quoting from recently published Proposed A.S.T.M. Specifications for a Cast Heat-resisting Alloy:

> If, as a result of agreement by the manufacturer and the purchaser, it is decided that the intended application is so critical that a creep test is necessary, it shall be made on each heat of alloy. Because of the inevitable difference of composition among nominally similar heats the testing of one or more heats selected as representative of a larger group will provide little indication as to whether or not the other heats will meet the requirements. The creep characteristics of alloys covered by these specifications are significantly affected by relatively small differences in composition. This sensitivity militates against the use of chemical composition as an acceptance criterion and also makes it necessary to exercise caution in the use of 'certified' creep data. The apparent variations in analysis frequently shown by reports from different laboratories on the same material, may be sufficient, if actually representative of differences of composition, to account for a variation of 100 per cent in actual limiting creep stress . . .

Thus is eloquently expressed a fundamental difficulty confronting those who would control creep in specifications for commercial metal products. The difficulty is further emphasized by the same Proposed Specifications:

> The time factor in creep testing tends to cause serious delay between production and acceptance. Some creep tests may require at least 1000 hr. to establish the minimum rate with assurance. Others may attain this rate in a few hundred hours. Moreover, if the preparatory work such as the selection of test material, machining and installation of test specimens, as well as the precision adjustments of creep furnace temperature is to be done with the care necessary for the obtaining of valid creep data several additional days may elapse.

Here indeed are serious practical difficulties where it is necessary to base stress design up to a limiting creep stress. The question might be properly asked, Why not incorporate various short-time test criteria of creep resistance in the commercial specifications? That acceptable correlations between short-time and long-time test methods are not yet at hand is expressed at the conclusion of a recently published report of researches on this subject by the Joint A.S.T.M.-A.S.M.E. Committee on Effect of Temperature on Properties of Metals:

> Although the results of this investigation do not emphasize the point, there is a great need for a short-time test which will predict structural changes which markedly affect long-time properties. The eventual development of a reliable short-time test must necessarily evaluate this factor.

It is significant to remark at this juncture that the A.S.T.M. Committee, promulgating the quoted proposed specifications for cast alloy in recommending advancement to "Tentative" status, deleted all reference to creep testing and creep-strength requirements. This decision was reached after several years of painstaking consideration, and serious debate.

DESIGN FOR STRESS

In view of the current pessimistic outlook regarding the rationalization of creep design from the materials procurement angle, the problem stands as a serious challenge before this symposium. A particularly serious aspect is presented when the specific consideration is nonferrous metals and alloys. These materials being economically at a premium, as they are in most instances, impels the stress designer to attempt the realization of the utmost from a minimum of material. This tendency has led to some flagrantly overstressed designs. Failures of materials to come up to the values assumed by the designers have led to some unhappy results. Owing to such practice, certain materials that might have given a satisfactory account in service, if conservatively applied, have been discredited in engineering practice in a way that is difficult to "live down."

Overstressing of metals under creep conditions is indeed hazardous. The same thermal activity that promotes creep usually leads to structural reorganizations and chemical interchanges. To such instability, the "cataclysmic" kind of failure is usually to be attributed, rather than to "out-of-bound" deformation. The intergranular separations and penetrations that are the work of chemical processes, experience has shown, are by far more insidious deterrents than is creep deformation *per se*.

While strict attention to infinitesimal creep rate is vital to the design of precision parts, design against failure by rupture should rest upon actual criteria of rupture. To this end, the Stress-Rupture Test is assuming an important engineering significance. This test usually will discriminate between materials that are stable and those that are susceptible to early failure by intergranular separations. The satisfactory "proofing" of materials may be accomplished through stress-rupture tests for numerous compositions, using short-time correlations. It is of interest to note that the same A.S.T.M. Tentative Specifications, previously discussed, although deleted of creep-limit requirements, as commercially impractical, do contain an elective 16-hr. stress-rupture test, which will rule out much unstable material not detected in thousands of hours of creep testing.

Creep testing is apt to be conducted to show the rates of creep to be anticipated at nominal design stresses. Nominal design stress, however, often does not anticipate the stress concentrations existing in most structures. It is at such points that intergranular failures generally have their inception. Therefore, designers should be critical not only on the score of adequate creep strength but also of the integrity of the material under stress well beyond the nominal design limits.

After two decades of creep testing, engineers and metallurgists fortunately are entering a new phase of sophistication upon the subject. The extreme duties to which metals have been pressed in new technologies have resulted in certain failures and deteriorations under stress of serious industrial proportions. These failures are not of the kind attributable to lack of cognizance of creep properties so much as to the lack of knowledge of structural instability factors. Some engineers, in retrospect, have expressed a feeling of "missed-the-boat" regret over too much concern about creep-rate studies and not enough investigation on structural instability. It has become increasingly apparent that the relationship between chemical environment and the stress design of metal structures are inseparable practical considerations that must be met in present day engineering.

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Creep of Nonferrous Metals and Alloys

1. C. R. Austin and J. R. Gier: Comparative Studies of Creep of Metals (Iron, Nickel, Cobalt, Silver, Iron-chromium-nickel Alloy, and Iron-chromium-silicon Alloy)

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* Compiled by Helen Basil, Crane Co. Research and Development Laboratories Library.

Using a Modified Rohn Test. *Trans.* A.I.M.E. (1934) **111**, 53–73; discussion, 73–74.

A modification of the Rohn test has been used to investigate the creep properties of iron (99.967 per cent), nickel (98.78 per cent), cobalt (99.32 per cent), fine silver and some ferrous alloys. The effect of the method of application of the load on test results is examined. At the higher temperatures the effects of minute amounts of plastic deformation on resistance to further creep become of less importance. Methods for obtaining derived curves that show the results more clearly are described, and the advantages of the methods are emphasized.

2. W. A. Baker: Creep of Non-ferrous Metals and Alloys. A review of published information. British Non-Ferrous Metals Research Assn. Research Report, Association Series No. 449 (June, 1937) 20 pp.

A summary of published information. Data have been selected critically, and include those for copper and its alloys, nickel alloys, aluminum and its alloys, and lead. The numerical values are tabulated, with compositions of materials. After each table appears a list of papers from which data were obtained, with a note on the content of each paper.

3. Creep Data. Compilation of available high-temperature creep characteristics of metals and alloys. Amer. Soc. Test. Mat. and Amer. Soc. Mech. Engrs. (1938). 848 pp.

Compiled by the creep-data section of the Joint Research Committee on the Effect of Temperature on the Properties of Metals. Standard tabulated forms are reproduced reporting creep-test results from 22 cooperating laboratories on 333 samples of wrought and cast ferrous materials and 55 nonferrous materials. Logarithmic curves of stress and corresponding creep rate are plotted, and for many materials curves of creep rate against temperature are also included.

Data on nonferrous materials (p. 713–848) include logarithmic curves of creep rate for 13 wrought copper-base alloys at 12 temperatures between 300° and 932°F. (150°–500°C.) inclusive; for nickel at 800° and 1000°F. (425°–540°C.) and for duralumin at 302°, 482°, and 662°F. (150°, 250°, and 350°C.); for 15 cast copper-base alloys at nine temperatures between 300° and 900°F. (150° and 480°C.); and for 25 specimens of lead and lead-rich alloys at 110°F. (43°C.).

In the foreword it is emphasized that extrapolation of creep-test results to longer periods than have been studied is not justifiable, particularly at the higher stresses and temperatures. Factors that may influence creep rate, particularly of ferrous materials, are outlined, and the application of the creep data to engineering design is briefly indicated.

4. C. H. Desch: Metals as Engineering Materials. Jnl. Roy. Soc. Arts. (1940) **88** (4561), 591–632; also *Engineering* (1940) **149**, (3866), 176–177; No. 3868, 231–232; No. 3871, 312–313.

A series of three Cantor lectures. Reviews the development and uses of metals as engineering materials. Part I deals with the historical development of metals and alloys, and indicates how engineering demands have stimulated metallurgical research, which, in turn, has contributed greatly to engineering progress. Part II discusses the methods of testing engineering materials. The importance is stressed of truly assessing service conditions and of examining the property of the material that has the greatest influence on its life under those conditions. In this respect it is pointed out that the suitability of materials for use in engineering at high temperatures is largely determined by their *resistance to creep*, while in high-speed machinery, fatigue testing is playing an increasing part. The importance and influence of alloying in improving the mechanical and the corrosion and wear-resisting properties of metals is discussed. Part III deals with the structures of metals and alloys, and discusses the effect of heat-treatment upon structure and upon physical and mechanical properties. Reference is made to powder metallurgy for the production of cutting tools, dies, porous bearings, etc.

5. S. Dushman, L. W. Dunbar, and H. Huthsteiner: Creep of Metals. *Jnl. Applied Physics* (Feb. 1944) **15**, 108–124.

Rates of creep were measured at temperatures ranging from 500° to 1500°, depending upon the conditions required for obtaining a constant rate of creep, to which this investigation was confined. An ingenious "interferometric" method of recording photoelectrically the slower rates of creep is described. Rates observed ranged from 6×10^{-6} to 6×10^{-3} cm. per min. Results of Fe alloys were erratic because of chemical changes irrepressible at high temperatures in the presence of N_2 and impurities in the metal. Eyring's theory of shear rates as applied to viscous flow is adopted as the basis of the theoretical work. Experimental results on wires are given for constantan; pure Al; 98 per cent Al, 2 per cent Mg alloy; commercial Al; Pt, Ni-Mo alloy and Ag. Creep data are quoted from the literature and reconsidered in terms of the theory presented, for polycrystalline Sn, Pb and for single crystals of Sn and Cd. Data on small Cu cylinders (0.16 to 0.5 in. dia.) are also presented. Au could not be studied by this theory because no conditions could be found where constant creep rates were obtained. Micrographs are shown for Al, Al-Mg and Ag, which demonstrate the relation between grain structure and rate of creep.

6. H. W. Gillett: Some Things We don't Know about the Creep of Metals. *Trans.* A.I.M.E. (1939) **135**, 15–58. (94 references).

Henry Marion Howe Memorial lecture. A general review of problems in connection with creep phenomena. The inadequacy of short-time tests is emphasized; most of the examples refer to ferrous alloys.

7. J. McKeown: The Creep of Metals (with particular reference to nonferrous metals). *Metal Industry* (London) (1940) **56** (15), 325–328; No. 16, 353–356.

A paper read before the London Local Section of the Institute of Metals. McKeown gives a short account of the whole subject of creep and deals with the representation of creep data, life under creep conditions, and short-time methods of creep testing, pointing out the limitations of these methods.

8. A. Pomp and W. Laenge: Rate of Creep of Metals under a Constant Load. *Mitt. K-WI. Eisenforsch.* (June 1936) **18**, 51–63.

   The results of creep tests on copper at 30°, 40°, 55° and 70°C., on zinc at 25°, 40°, 55° and 70°C., and on lead at 30°C. are shown in a series of graphs. No periodicity in the elongation curves due to the conjunction of hardening and recrystallization phenomena was observed with any of the metals. Recommendations are made for standard conditions for short-time creep tests on these metals.

9. Report of Committee B-4 on electrical heating, electrical-resistance and electric furnace alloys. Amer. Soc. Test. Mat. Preprint, 1944.

   This paper contains an appendix stating the considerations of creep-testing requirements for the commercial acceptance of materials.

10. F. Sauerwald: Relation between Load and Elongation Velocity in Creep Stresses. *Archiv Eisenhüttenwesen* (1943) **16**, 269–272.

    Curves of stress-elongation velocity in creep tests were taken. The occurrence of a discontinuity point (in logarithmic plotting) was observed in all technically important metals (steel, Pb, Al, Mg, Cu and Sn); the location of this is a measure for the creep strength. The branch of the curve with the higher elongation velocity has a stronger dependence on temperature and steel composition. The occurrence of the discontinuity point is mainly connected with the condition that, for low stresses, a general flow of the material is prevented because of the polycrystalline structure and the increased strength caused by stresses. Under high loads, the high creeping velocities are caused especially by active formation of gliding planes.

11. Symposium on Effect of Temperature on the Properties of Metals. Held at joint meeting of Amer. Soc. of Mech. Engrs. and Amer. Soc. for Test. Mat., Chicago, Ill., June 23, 1931. 829 pp.

    Creep of ferrous metals mostly discussed. Creep of copper and its alloys, by J. J. Kanter, pp. 363–366. Creep of nickel and nickel alloys, by C. A. Crawford and R. Worthington, pp. 557–588.

Aluminum and Aluminum Alloys

12. H. Adenstedt: Creep Behavior of Some Al-Cu-Mg and Al-Zn-Mg Alloys between 25° and 300°. *Aluminium* (1943) **25**, 13–19.

    With an especially devised apparatus for the observation of creep behavior of light metals, five materials of the type Al-Cu-Mg (Din 1713), 3 Al-Zn-Mg alloys and one Al-Cu-Zn-Mg alloy were investigated with respect to their time elongation limit (0.2 per cent permanent elongation in 200 hr. loading time) in the temperature range 25°–300°. Up to 80°, the Al-Zn-Mg alloys (after hot-pptn.) possesses the best mechanical strength; for higher temperatures, however, the much higher heat strength of the Al-Cu-Mg alloys becomes evident; even for as low as 3 per cent Cu contents equally good creep strengths were observed in the latter alloys at average and higher temperatures. The Cu-poor alloys could, however, not be brought again by hot-pptn. hardening to a high-cold-elongation limit. The time-elongation limit of an Al-Zn-Cu-Mg alloy was between the scattering ranges found for Al-Zn-Mg and Al-Cu-Mg. A fine grain seems to be unfavorable at high temperatures for the creep strength.

13. E. Hottenrott: Creep Strength of Dural Sheet Rivets. *Luftfahrtforschung* (1940) **17**, 247–249.

    Report on investigations carried out on creep strength of Dural-riveted joints of six different kinds. Determining factors for explanation of differences in creep-strength values are recapitulated. General importance of these preliminary experiments is briefly dealt with.

14. Irmann and W. Mueller: Determination of Creep limit of Aldrey and Pure Aluminum. *Aluminium* (1935) **17**, 7–10.

    Tests carried out on aluminum and Aldrey by the accelerated creep method of Pomp and Hoeger show that the method gives results a little lower than those obtained in prolonged endurance tests provided that the test is made over a period of 25–35 hr. and that the rate of elongation is about 0.0012 per cent hr. Aldrey with a breaking strain of 35.4 kg. per sq. mm., has an endurance strength of 29.9 kg. per sq. mm.; hard-drawn aluminum with a breaking strain of 19.3 kg. per sq. mm. has an endurance strength of 12.8 kg. per sq. mm.

15. R. R. Kennedy: Creep Characteristics of Aluminum Alloys. *Proc.* Amer. Soc. Test. Mat. (1935) **35**, pt. II, 218–231.

    Before loading specimens were "stabilized" at the test temperature as follows: 68 hr. at 205°C., 20 hr. at 315°C. Sensitivity of strain measurement 4×10^{-6}, particles of precipitated intermetallic compound were clearly visible in the microstructure of alloy No. 2 after creep testing for 500 hr. 205°C. The particle size increased markedly after testing 300 hr. at 315°C.

    The stresses producing creep rates of the order of 10^{-6} strain per day were considerably lower than the limit of proportionality (determined at the test temperature after "stabilizing" as for creep specimens).

    The author observed some correlation between creep characteristics and service behavior in the case of air-cooled cylinder heads for aero-engines. These parts cast from alloy 1 and 2 proved satisfactory, but heads of the same type cast from alloy No. 8 failed in block test of the engine. Alloy No. 8 has a low thermal conductivity, and in consequence the working temperature of these heads is approximately 28°C. higher, which may of course contribute to the failure. Aero-engine pistons, formerly cast from alloys 1 and 2, are now forged from alloys 5 and 7, and, despite the comparatively poor creep characteristics of the two latter, the wrought pistons have given satisfactory service. Again a difference in operating temperature may be a contributing factor, since, due to changes in design, the wrought pistons operate cooler than do the cast type.

16. J. Marin and L. E. Zwissler: Creep of Aluminum (Alloy) Subjected to Bending at Normal Temperatures. Amer. Soc. Test. Mat. Preprint No. 43 (1940) 10 pp.

Measurements of creep deflection in bending were made on four specimens of 3S-½ H aluminum alloy (1.2 per cent Mn) at room temperature for periods up to 400 hr. Tension creep tests were also carried out on the same material. An expression relating creep deflections in bending and in tension is developed, and reasonably good agreement is obtained with that given by the experimental values.

17. W. Mueller: Creep Strength of Stabilized Wrought Aluminum Alloys. Nat. Advisory Committee for Aeronautics *Tech. Memo* No. 960 (Nov. 1940) 6 pp., 8 supp. sheets.

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18. H. J. Tapsell, A. E. Johnson and W. J. Clenshaw: Properties of Materials at High Temperatures. D.S.I.R. Engineering Research, Special Report No. 18 (1932). The sensitivity of strain measurement was 5 × 10^{-5}.

The strength at high temperatures of six steels and three nonferrous metals.

19. Unpublished B.N.F.M.R.A. Work.

Straight lengths of hard-drawn wire, 0.16-in. dia., were tested at room temperature, which was subject to seasonal fluctuations. The extensometer compensated for thermal expansion and contraction of the specimen, and the sensitivity of strain measurements was 5 × 10^{-6}.

20. A. Von Zeerleder and R. Irmann: Industrial Metallic Materials at Elevated Temperatures. With special reference to the behavior of aluminum and its alloys. (In German.) Int. Assn. for Test. Mat. *Proc.* London Congress, 1937, Group A, 23–26.

Mechanical properties of pure aluminum, Avional, Anticorodal, and other industrial aluminum alloys, were measured between 20° and 250°C., after annealing the test specimens at the same temperature for various periods up to 540 days.

Copper and Copper Alloys

21. J. W. Bolton: Some Tests on Tin Bronzes at Elevated Temperatures. *Proc.* Amer. Soc. Test. Mat. (1935) **35**, pt. II, 204–212.

The alloy specified in A.S.T.M. standard specifications for steam or valve bronze sand castings (B-61)[2], an essentially solid-solution structure, is shown to have a "limiting creep strength" of about 8000 lb. per sq. in. at 500°F. and to be free from embrittlement. At 600°F. the alloy has low "creep strength" and is of low ductility after exposure to this temperature for long periods.

The alloy specified in A.S.T.M. standard specifications for sand castings of the alloy containing Cu, 88 per cent; Sn, 8; Zn, 4 (B-60)[3] (the composition, Cu 88 per cent, Sn 10, Zn 2 falling within this specification is the one specifically referred to) consists of an essentially solid solution matrix, throughout which a high tin component (the alpha-delta eutectoid) is dispersed in small particles.

This alloy's load-carrying characteristics at 500°F. are inferior to alloy B-61, and there is evidence of embrittlement under exposure to a temperature of 500°F. Microscopic study, especially of material exposed to a temperature of 600°F., shows clearly that this embrittlement is due to formation and possibly to penetration of the brittle eutectoid structure along grain boundaries.

22. H. L. Burghoff, A. I. Blank and S. E. Maddigan: Creep Characteristics of Some Copper Alloys at Elevated Temperatures. *Proc.* Amer. Soc. Test. Mat. (1942) **42**, 668–689; discussion, 690–691.

Results are reported of creep tests at 300°, 400° and 500°F. (149°, 204° and 260°C.) on seven wrought copper alloys: 70-30 brass, silicon-bronze (3 per cent Si), 85-15 brass, Naval brass, Admiralty brass, phosphor-bronze (5 per cent Sn), and 70-30 cupronickel. The 70-30 brass was studied in greater detail than the rest. The alloys were prepared in various tempers in order to determine the effect of grain size in the annealed tempers and that of degree of reduction in hard tempers. The tests were made on specimens of wire 0.125 in. in diameter, with a gauge length of 10 in., in three forced-convection, multiple specimen furnace. The duration of most of the tests was of the order of 5000 hr., though some tests of special interest were continued much longer.

The character of some of the creep curves obtained demonstrates the wisdom of extending creep-testing periods as long as possible. It was found that grain size and degree of cold-working are important factors in determining the creep resistance of these alloys, and in general are fully as important as chemical composition. The creep resistance of annealed 70-30 brass for feasible stresses increases with grain size at 300°, 400°, and 500°F.; this is partly in agreement with published information, but reduces the known temperature at which coarser grained material becomes superior to fine-grained material of this composition.

The creep resistance of these alloys, finished by a cold-working operation, is largely determined by their recrystallization characteristics; if they recrystallize within a short time at elevated temperatures, they behave as annealed materials; if recrystallization takes place over a long period, the material may be very unstable in respect to creep; if no recrystallization occurs, the creep resistance may be high, but, on the other hand, intercrystalline parting may embrittle the metal. In the last case recrystallization will probably begin after an exceedingly long time. Very coarse-grained material, either as annealed or as cold-worked, may become embrittled and liable to sudden failure under conditions where it appears to offer high resistance to creep. The 70-30 copper-nickel alloy is easily the best of the alloys tested for service at high temperatures.

23. C. L. Clark and A. E. White: Influence of Recrystallization Temperature and Grain Size on Creep Characteristics of Nonferrous Alloys. *Proc.* Amer. Soc. Test. Mat. (1932) **32**, pt. II, 492–506; discussion, 507–516.

The specimens were held at test temperature one day before loading. Load was applied in increments until creep began, and was then maintained constant until creep ceased or remained constant for at least 200 hr. The load was then increased, and the process repeated until at least four creep rates had been measured; sensitivity of strain measurement 2.8×10^{-6}.

The lowest temperature of recrystallization was determined by hardness tests, on severely cold-worked specimens, before and after annealing 100 hr. at various temperatures. The results were confirmed by metallographic examination, and were as follows:

Alloy	Recrystallization Temperature Range, °C.
Cu-Zn 85-15	260–315
Cu-Zn 70-30	205–260
Cu-Zn-Sn 70-29-1	205–260
Cu-Zn 60-40	150–205

Micrographic examination of creep specimens of 70-30 brass (hot-rolled to ⅞ in., cold-drawn to ¾ in.) revealed that

a. Below the recrystallization temperature no apparent structural change occurred in 2000 hr.

b. Just above this temperature recrystallization and grain refinement had occurred in 1600 hr.

c. At higher temperatures grain growth was also apparent after 500 hr.

The authors concluded that:

1. Below the recrystallization temperature the alloys withstand appreciable stresses without continuous deformation, within the limits of strain measurement. At temperatures just below this range the limiting stress approximates to the limit of proportionality at the temperature, except in cold-worked materials. In the cold-worked alloys the stress for no flow was rather lower than the limit of proportionality.
2. Above the recrystallization temperature continuous creep occurred at very low stresses and probably would occur at any stress.
3. The slope of the log stress (ordinate)-log. creep rate (abscissa) curve increases as the recrystallization temperature is passed. Below this temperature the curves for the various alloys were approximately parallel, but were not necessarily so above this temperature.

24. C. L. Clark and A. E. White: Properties of Nonferrous Alloys at Elevated Temperatures. *Trans.* Amer. Soc. Mech. Engrs. (1931) **53**, 183–189; discussion, 189–191.

The method of test and the sensitivity of strain measurement were the same as those described in ref. 23.

25. C. C. Davenport: Correlation of Creep and Relaxation Properties of Copper. *Jnl. Applied Mechanics* (A.S.M.E.) (1938) **5** (2), A55-60.

Creep tests and relaxation tests were carried out in torsion on copper tubes, which permit a verification of the various theories proposed for a deduction of the relaxation characteristics from creep tests alone. It was found that the relaxation time actually observed lies between the two values calculated for this quantity on the basis of the strain-hardening and the time-hardening theories.

26. E. A. Davis: Creep and Relaxation of Oxygen-free Copper. *Trans.* Amer. Soc. Mech. Engrs. (1943) **65**, A-101-5; discussion A-240-2.

This paper contains results of creep and relaxation tests on an oxygen-free copper at temperatures up to 235°C. The effect of the stress and the temperature upon the strain rate has been noted and an effort has been made to correlate the results of the two different types of tests by using various theories of plastic deformation.

27. V. Jareš and L. Jeniček: Mechanical Properties of Hard-drawn Copper Wire under Continuous Loading at Elevated Temperatures. (In German.) Int. Assn. for Test. Mat., *Proc.* London Congress. (1937) A-17-20.

A study was made of the softening at elevated temperatures of hard-drawn wires of electrolytic copper, with particular reference to the time factor. Hard and semihard wires of 5-mm. diameter were heated (unloaded) for periods from ¼ to 256 hr. at temperatures varying from 175° to 400°C. and were then tested to fracture at room temperature. Above 275°C. softening was almost complete; after heating for ¼ hr. below 275°C. the softening depends widely on the duration of heating, and is attained after sufficiently long heating even at 175°C., the softening occurring slightly more rapidly in the harder wires. It is remarkable that the modulus of elasticity does not begin to change until considerable softening has occurred. The softening is accelerated by even a small continuous loading during the annealing process. Above 250°C. the wires begin to flow under the continuous loading, the critical temperature being sharply defined and corresponding with the equicohesive temperature.

28. C. H. M. Jenkins, E. H. Bucknell and E. A. Jenkinson: Interrelation of Age-hardening and Creep Performance, pt. II. Behavior in Creep of an Alloy Containing 3 per cent Nickel and Silicon in Copper. *Jnl.* Inst. Metals (Feb. 1944) **70**, 57–79.

An investigation has been made into the behavior under creep conditions of a wrought copper alloy containing 2.4

per cent Ni with 0.6 per cent Si, after different thermal treatments. These bring about aging in the alloy and render possible a comprehensive survey of its properties in relation to various amounts of either age-hardening or age-softening in the range 15°–625°C.

The results of tests carried out for short and long times show that at certain temperatures the ability of the alloy to withstand stress varies widely as the result of different heat-treatments. In long-time tests between 230° and 600°C., fully age-hardened material is markedly inferior to fully softened material, but in short-time tests the converse holds.

The changes in microstructure of both stressed and unstressed specimens of the alloy in its various conditions are compared. It is found that the rupture of tensile and creep specimens in the range 300°–500°C. results from the development in intercrystalline cracks, whereas at lower temperature transcrystalline fractures are found. In fully softened material there is, however, appreciable lengthening of the crystals before the intercrystalline form of cracking begins to develop.

29. J. J. Kanter and E. A. Sticha: Creep Rate from Tests of Short Duration. *Trans.* Amer. Soc. Metals (1940) **28**, 257–271; discussion 271–276.

A number of papers have been presented dealing with the subject of short duration tests to serve the purpose of verifying materials for use at elevated temperatures. It is a serious problem among testing engineers to develop some suitable acceptance tests for materials to be used at elevated temperatures which reliably indicate good creep properties. Obviously, the execution of actual creep tests is such a lengthy and expensive process that as such they cannot serve for acceptance testing purposes. Clark and White have proceeded upon the basis that a relationship exists at a constant temperature between the long-time and short-time rupture properties of steels, studied with load as the variable.

In the present paper a correlation is suggested from another standpoint which may for some purposes be more convenient. It is attempted to show that for a given load condition relationship between short and long-time creep rates can be established with temperature as the variable. For various theoretical reasons it is held that the temperature variable is a much more fundamental one to study and possibly affords more promise in establishing a reliable long-time short-time correlation than does the load variable into which many more complex influences enter (most of the results given relate to ferrous materials, but there are a few data for a wrought copper-base alloy containing aluminum 7.0, silicon 2.3 per cent).

30. E. R. Parker and C. Ferguson: Rupture Tests at 200°C. on Some Copper Alloys. *Trans.* Amer. Soc. Metals (1943) **31**, 699–714; discussion, 714–715.

Rupture tests at 200°C. (390°F.) were made on several copper-base alloys. Stress-life curves are given, and micrographs of short-time and long-time fractures. It was found that:

1. The strength of tough-pitch copper drops off rapidly with time. The 1000-hr. strength is only half of the short-time strength.
2. Small additions of certain metals greatly increase the long-time strength without increasing the short-time strength appreciably.
3. At 200°C. (390°F.) cold-worked, precipitation-hardened copper alloys are much stronger both in short and long-time tests than tough pitch copper.
4. At 200°C. (390°F.) there is a great difference in strength between hardened cobalt beryllium copper and beryllium copper. However, at 350°C. (660°F.) the difference is much less, probably because beryllium copper overages at this temperature while cobalt-beryllium copper does not.
5. Intercrystalline cracking in copper at 200°C. (390°F.) may be reduced or possibly eliminated by small additions of certain elements such as silver, manganese, cadmium or chromium.

31. E. R. Parker and C. F. Riisness: Effect of Grain Size and Bar Diameter on Creep Rate of Copper at 200°C. *Trans.* A.I.M.E. (1944) **156**, 117–124.

Creep tests at 200°C. were carried out on copper of 99.988 per cent purity, using bars of 0.160, 0.375 and 0.505 in. diameter. By suitable working and annealing treatments the grain size was made to vary from 3 to 1500 grains per sq. mm. Experiments with the thinnest bars at first suggested that there was an optimum grain size that gave a minimum creep rate, but this effect was found to be due to oxidation of the specimen, and experiments with cadmium-plated bars showed that the grain size has little effect on the creep rate. Curves are reproduced showing the diamond pyramid hardness of the copper after cold-working and annealing for 20 hr. at different temperatures. It is suggested that 200°C. is a critical temperature, at which opposing effects cancel so far as concerns the effect of grain size on creep rate.

32. H. J. Tapsell and A. E. Johnson: Properties of Copper in Relation to Low Stresses. Pt. II. Creep tests at 300°C. and at 350°C. on arsenical copper and silver arsenical copper. *Jnl.* Inst. Metals (1932) **48**, 89. (B.N.F.M.R.A. Reports, 1930, R.R.A. 274 and 276).

Sensitivity of strain measurements 5×10^{-6}. The authors concluded from the stress-log creep-rate curves that silver arsenical copper would be even more superior to arsenical copper, in respect to creep resistance at 300° and 350°C., at stresses less than 2 tons per sq. in. (i.e., at rates of creep equal to or less than 10^{-5} strain per day) than at higher stresses.

33. H. J. Tapsell, A. E. Johnson and W. J. Clenshaw: Properties of Materials at High Temperatures. The strength at high temperatures of six steels and three nonferrous metals. D.S.I.R. Engineering Research, Special Report No. 18 (1932). Sensitivity of strain measurement 5 ×

10^{-5}. The phosphor-bronze specimens tested at 150°C. gave abnormal creep curves. At intervals the specimens, after creeping steadily for 10–50 days, yielded abruptly and then continued to creep at rates similar to those before yielding. These sudden strains were comparatively large, varying from 0.02 to 0.06 in. per inch.

34. Unpublished Work (British Non-Ferrous Metals Research Assn.), 1936.

Straight lengths of hard-drawn wire, 0.16-in. diameter, were tested at room temperature, which was subjected to seasonal fluctuations. The extensometer compensated for thermal expansion and contraction of the specimen and the sensitivity of the strain measurement was 5×10^{-6}.

35. A. E. White and C. L. Clark: Influence of Grain Size on High-temperature Characteristics of Ferrous and Non-ferrous Alloys. *Trans.* Amer. Soc. Metals (1934) **22,** 1069–1088; discussion, 1089–1098.

Results show the influence of both the McQuaid-Ehn (inherent grain size and the grain size as produced through heat-treatment (actual) on the high-temperature characteristics of metals. For the inherent grain-size studies two ferrous alloys were used, one of which contained 0.50 per cent Mo and the other 0.25 per cent Mo and 1.25 per cent Mn. For actual grain-size investigations two nonferrous alloys of the copper-zinc-tin type were used, which differed in amounts of copper and zinc they contained. Tests on nonferrous alloys were limited to tensile tests at room and elevated temperatures and to creep tests at temperatures of 300° to 600°F. (150° to 315°C.).

Lead and Lead Alloys

36. J. B. Baker, B. B. Betty and H. F. Moore: Creep and Fracture Tests on Single Crystals of Lead. *Trans.* A.I.M.E. (1938) **128,** 118–138.

Single crystals of very pure commercial lead were submitted to creep tests, fatigue tests using repeated axial tensile stress (range zero to maximum), and ordinary tensile tests. An empirical resolved shear stress of approx. 250 lb. per sq. in. was determined. Any stress above this caused relatively rapid creep in the single-crystal specimen, while in short-time tensile tests, elongation increased at an accelerated rate above this stress. In the repeated tension fatigue tests, this critical resolved shear stress marked approximately a boundary below which specimens withstood 300 million cycles of stress without fracture, and above which they withstood less than 4 million cycles. The shapes of the creep-time curves for single crystals and for polycrystalline lead resembled one another closely. If the original orientation of the crystal is such that one of the resolved shear stresses on an octahedral plane is much larger than the others, slip takes place on the plane concerned in the direction of the predominant resolved stress, with the formation of slip-bands. Successive slip stages occur, and the crystal settles down into a state with a balanced stress system in which slip takes place in different directions. If the orientation is such that a balanced shear stress system was present originally, deformation may occur without the formation of visible slip lines. X-ray evidence of the formation of crystallites on atomic planes is given, and the conditions of final fracture are discussed.

37. J. N. Greenwood and C. W. Orr: Influence of Composition on the Properties of Lead. Pt. VIII—The Influence of Copper. *Proc.* Australasian Inst. Min. and Met. (1938) **109,** 1–24.

As little as 0.007 per cent Cu can be detected microscopically in cast rolled lead; up to 0.06 per cent Cu remains evenly dispersed as fine particles of eutectic throughout the alloy, but with larger amounts primary copper crystals are formed and these have a strong tendency to segregate.

The creep rate of pure lead is increased by addition of up to 0.01 per cent Cu, but larger additions cause a rapid decrease in this rate, which reaches a minimum at 0.06 per cent Cu. Vibration superimposed on stress appreciably increases the creep of lead, but the effect is considerably reduced by the presence of copper in the lead, 0.07 per cent Cu reducing the rate by 90 per cent under 350 lb. per sq. in. Lead containing a minimum of 0.06 per cent Cu stretches less than 1 per cent in the first year under 350 lb. per sq. in. with vibration and thereafter less than 0.5 per cent per annum. Pure lead behaves similarly only when the stress is less than 200 lb. per sq. inch.

38. J. N. Greenwood and H. K. Worner: Influence of Elements on Properties of Lead. Pt. VII—Influence of Composition on Creep rate of Industrial Lead. Australasian Inst. Min. and Met. (1936) **104,** 385–419; discussion 420–422.

The lead used in this investigation contained in thousands per cent: Ag 0.3, Cu 0.2, Bi 2.3, Zn 0.5, Sb 4.2, Fe 0.7, Cd 0.1, As 0.02, and S 0.4. The rate of creep of this lead after melting in air was much less than that of electrolytic lead (0.0005 per cent total impurities); when the metal was annealed at 120°C. for 24 hr. and tested 3 hr. after quenching, the specimen broke much earlier than a similar specimen tested 3 weeks after quenching, and the fracture was intercrystalline instead of ductile. Addition of silver up to 0.1 per cent to the lead increased the hardness and resistance to creep and decreased the grain size after rolling; with 0.01 to 0.05 per cent Ag the creep rate (50–100 days) is 3×10^{-5} in. per in. per day under 350 lb. per sq. in. of stress in the annealed state. Addition up to 1 per cent Sb to the lead had little influence on the hardness or on the rate of creep, but the latter was about three times that of the corresponding silver alloy; the 0.1 per cent Sb alloy breaks eventually in an intercrystalline manner, while the 0.01 per cent alloy is very sensitive to grain growth on annealing. A small increase in the bismuth content of this lead caused a marked initial increase in the rate of creep of the rolled metal but this effect was decreased with more bismuth; the effect of the annealed metal was slight. Creep of the alloy with 0.1 per cent Bi under 350 lb. per sq. in. was 7 × 10^{-5} in. per in. per day. Bismuth had little effect on the grain size after rolling, but the 0.005 per cent alloy was very sensitive to grain growth on annealing. Zinc had a somewhat similar, but more irregular and less marked effect than silver on the creep of this lead.

39. J. N. Greenwood and H. K. Worner: Types of Creep Curves Obtained with Lead and its Dilute Alloys. *Jnl.* Inst. Metals (1939) **64**, 135–158; discussion 158–167.

It is shown that four distinct types of creep curves are obtained with lead and its dilute alloys under stresses of 350 and 500 lb. per sq. in. Type A shows strain-hardening, and after a certain stage there is a marked increase of creep rate owing to recrystallization. Type B shows initially an increase in creep rate and then strain-hardening, but no recrystallization. This type is accompanied by intercrystalline failure. Type C shows a continuously increasing creep rate, which is held to be associated with loss of cold-working hardness during the test and also with an increase in the proportional limit as compared with the basis lead. Type D is a normal strain-hardening variety, characteristic of metals that are below the recrystallization range of temperature. Curves are given illustrating the effects of stress and composition, initial cold-working and grain-size. In both the latter, the examples are merely to indicate complexity and are not exhaustive. In a theoretical section, it is suggested that creep has two components: (1) viscous flow, and (2) plastic flow. In the range of low stresses and with cold-worked material, viscous flow is considered to be the more important. The proportional limit is suggested as an approximate point of division between high and low stresses for this purpose. The types of curve mentioned are considered in the light of this theory.

40. J. N. Greenwood: Influence of Impurities on the Properties of Lead. *Proc.* Australasian Inst. Min. and Met. (1934) No. 95, 79; (1935) No. 100, 477; (1936) 101, 57.

R. S. Russell: *Ibid.* (1936) No. 101, 33.

An extensive investigation on the influence of impurities in lead, now in progress at the University of Melbourne, includes an examination of the creep characteristics of lead and dilute lead alloys. These publications are progress reports of long-time creep tests, in which the creep resistances of the materials were assessed by comparing the creep rates produced by a given stress. The stress was in most cases 500 lb. per sq. in. and the creep rates, with a few exceptions, were very high, of the order of 10^{-3} strain per day. The tests so far conducted do not therefore provide the comparative data sought in this review.

41. J. McKeown: Creep of Lead and Lead Alloys. Pt. I—Creep of Virgin Lead. *Jnl.* Inst. Metals (1937) **60**, 201–222; discussion and correspondence, 223–228. References.

In room-temperature tests, the temperature varied from a maximum of 23.5°C. (summer) to a minimum of 12°C. (winter), but for the greater part of the time the temperature was between 15° and 18°C. The method of strain measurement compensated for thermal expansion and contraction, and the sensitivity of strain measurement was (1) ± 10^{-4} in tests at stresses greater than 300 lb. per sq. in., (2) ± 10^{-5} at lower stresses.

The author concluded from these tests that the grain size of extruded lead is a major factor determining its resistance to creep at room temperature. The resistance to creep decreases with decreasing grain size, the creep rate increasing rapidly as the average grain area falls below 0.1 sq. mm. The initial stage of rapidly decreasing creep rate was very marked in coarse-grained lead, but absent or nearly so from the curves for fine-grained specimens. Small amounts of cold-work, such as occur in flattening cable sheath and in bending pipes, caused a definite increase in the resistance to creep in the early stage of the test, the effect being most marked in the coarse-grained materials.

42. H. F. Moore and N. J. Alleman: Creep of Lead and Lead Alloys Used for Cable Sheathing. Univ. Illinois Eng. Expt. Sta. *Bull.* 243 (1932) 26 pp.

Creep tests made at 32° and 150°F. (0 and 65°C.) on pure lead and lead alloys containing 1, 2 and 3 per cent Sn, or 0.75 or 1 per cent Sb, or 0.04 Ca showed that continuing creep occurs with stresses as low as 150 lb. per sq. in., although the tensile strength of the materials is 1530 to 3850 lb. per sq. in. Short-time tensile tests on the calcium alloy showed that increased pulling speed increased the tensile strength values. No absolute creep limit was found for any of the metals tested, but graphs showing stress as ordinates and hours required to produce a 1 per cent creep as abscissas (log scale) showed a distinct flattening out tendency, and in some cases seemed to be approaching a horizontal asymptote. Tests made with an arbitrary method of determining a practical creep limit indicated that a value of 200 lb. per sq. in. may be deemed a fair average practical creep limit for this type of alloy at 32°–150°F. (0–65°C.). Increase of temperature accelerates creep at the higher stresses. Definite creep has been observed in full-size specimens under stresses of 200 lb. per sq. in., but the average rate of creep is less than in the test specimens.

43. H. F. Moore, B. B. Betty, and C. W. Dollins: Creep and Fracture of Lead and Lead Alloys. Univ. Illinois Eng. Expt. Sta. *Bull.* 272 (1935) 47 pp. (See also *Bull.* 243 and 306).

The materials used in this investigation were: commercially pure lead (A); and alloys thereof with 2 per cent Sn (B); 0.75 per cent Sb (C); and 0.04 per cent Ca (D). In no case is there an absolute limiting tensile stress below which no creep occurs; at room temperature under a stress of

180 lb. per sq. in. creep occurs at a rate varying from 0.3 per cent per annum for D to 0.6 per cent per annum for A, and at 65°C. the corresponding figures are 0.6 and 1.4 per cent. Extrapolated from the results of tests over 1000 hr. the approximate creep at room temperature under one year of steady tensile stress is as follows: 200 lb. per sq. in., (A) 0.7, (B) 0.6, (C) 0.4, (D) 0.3; 300 lb. per sq. in., (A) 1.6, (B) 1.1, (C) 0.7, (D) 0.4; 400 lb. per sq. in., (A) 3.9, (B) 1.9, (C) 1.0, (D) 0.6; 500 lb. per sq. in. (A) 5.0, (B) 3.2, (C) 1.4, (D) 0.8. These figures show that the addition of calcium and antimony has a very marked effect in reducing the creep of lead at high stresses. The lowest stress under which fracture occurs under long continued load is 600 lb. per sq. in. for A, B, and C and 1000 for D, the corresponding times to fracture being about 36, 148, 262 and 333 days, respectively. Under reversed flexural stresses of 200 lb. per sq. in. about 10^8 cycles are necessary to produce fracture of A, the weakest of the metals tested. Microscopic examination of lead and its alloys after subjection to long-continued steady loads indicate that there is distortion by rotation of at least the surface crystals, whereas in short-time tests distortion occurs by slip within the crystal grains, large-grained metal appearing, to resist creep better than fine-grained metal. In creep tests on single crystals distortion occurs along certain definite atomic planes and there appears to be a limiting resolved shearing stress along these planes below which creep is very slow, but above which it occurs rapidly.

44. H. F. Moore, B. B. Betty, and C. W. Dollins: Investigation of Creep and Fracture of Lead and Lead Alloys for Cable Sheathing. Univ. Illinois Eng. Expt. Sta. *Bull.* 306 (1938) 90 pp. (See also *Bull.* 243 and 272).

(I–II) Creep tests at low stresses, not exceeding 400 lb. per sq. in., were made on narrow flattened specimens, ¼ in. wide with a gauge length of 10 in. cut from 25 samples of sheathing furnished by manufacturers and users. The effect of flattening, although appreciable and variable is not considered to be of major importance and the test results probably are comparable with the behavior of a sheath after being handled in installation. The majority of tests were continued for 2000 hr. at a controlled temperature of 78°, 110°, or 150°F., but seven samples were tested for 7200 to 10,000 hr. at 110°F. The creep-time curves are reproduced. Derived curves are also given for: (1) the "minimum creep rate" against stress, and (2) the total creep (determined by the McVetty method) against stress. The McVetty total creep in 10,000 hr., based on a 2000-hr. test, is considered to be the most satisfactory measure of creep resistance. The calcium-lead alloys with 0.04 per cent Ca are most resistant to creep, and the antimony-lead and tin-lead alloys appear, on the whole, less resistant than pure or copper-bearing lead. Considerable variations were found in the creep resistance of apparently similar materials. The effect of temperatures between 78° and 150°F. on the creep resistance of 8 samples was studied, and the results are shown in isomeric creep rate-temperature-stress diagrams.

(III) Tests to fracture under higher stresses indicate that the tensile stress *TS* which breaks the specimen in time *t* can be related to the stress *TS′* which produces fracture in 10 hr. by the expression $TS = TS' - K\,(\log - 1)$. Superimposed small vibratory stresses of 30 lb. per sq. in. considerably reduce the time to fracture.

(IV) Tests in 8 types of reversed-bend and fatigue machines gave widely differing results with the same metal, according as to whether the specimen was subjected to severe bends (over 10°) or slight ones (less than 45′). Metals most resistant to creep show greatest resistance to many cycles of small stress; those which creep more rapidly withstand better the effects of a few severe bends.

(V) Tests on length of cable sheath under constant internal oil pressure were difficult to correlate with the creep tests on narrow specimens, probably on account of the indeterminate effects of dents and bends in the cable sheath. In general, cable sheaths appear to be more resistant to creep than would be predicted.

(VI) A discussion of the stresses produced in various types of oil-filled cables in service is given by Hermand Halperin, and reference made to a method of measuring dimensional changes by observations of the electrical capacitance of the cable.

(VII) A theory of creep in lead is briefly outlined. In the first stage of creep, work-hardening is considered to occur in the second, viscous or "quasi-viscous" flow occurs while in the third there is "fragmentation."

(VIII) In an appendix F. E. Edwards gives a mathematical analysis of the effect of eccentricity of the sheath on creep.

45. H. F. Moore and C. N. Dollins: Fracture and Ductility of Lead and Lead Alloys for Cable Sheathing. Univ. Illinois Eng. Expt. Sta. *Bull.* 347 (1943) 62 pp. (See also *Bull.* 243, 272 and 306).

Creep tests to fracture have been carried out at 21° and 43°C. on flattened samples cut from 35 lead and lead-alloy sheaths of underground electric cables. The results can be generally expressed as $S = S_1\,(1 - c\ 1gt)$, where S is the stress that will cause fracture in time t and S_1 and c are constants. The elongation at fracture tends to decrease in long-time tests, but the results showed considerable scatter. The more useful criterion of the allowable stress in service would probably be the elongation e_e, which would be produced if creep remained constant at the "second-stage" value (instead of being accelerated by "necking"), and for this index the name "creep ductility" is suggested. The results of the tensile creep tests correlated well with long-time bursting tests under hydraulic pressure made by the Philadelphia Electric Co. The effect of notches of different shape on creep endurance was studied; no appreciable weakening was observed in the softer materials. Fatigue tests under reversed bending, made on strip specimens of chemical lead and lead-calcium alloy, showed that a heavy coating of grease increased the fatigue endurance, probably chiefly by diminishing the stress intensity at the edges of the jaws. Further tests at frequencies of 1–148 cycles per minute indicated that fracture occurred in fewer reversals at the lower frequencies, probably as a consequence of creep. Little difference was found in the creep endurance between specimens cut longitudinally and transversely. Welds, although they seem to have enough weakening effect to locate the fracture in long-time bursting and tensile tests, do not diminish the measured tensile strength or elongation appreciably. Fine cracks which were observed in some lead-calcium specimens are believed to have been present in the sheath after extrusion. A few laboratory tests on the effect of superimposing a slight vibratory stress on the steady tensile load in creep tests have been inconclusive; tests in a manhole, however, indicate that severe vibration from traffic may reduce creep endurance appreciably.

46. W. G. C. Oxenaar: Alloy Lead Pipe. *Ingenieur's Gravenhage* (The Hague) (1941) **56**, (25), MK 35–39; *Chem. Abs.* (1943) **37**, 4672.

The composition of the lead alloys average was tin 0.7–1.1, antimony 0.05–0.15, and other metals less than 0.05 per cent. Investigations were carried out to determine which composition would have the greatest wall strength in pipe. Eight different alloys were tested for hardness, tensile strength, *creep strength*, and for the effect of annealing from 240°C. The tendency to precipitation-hardening is noticeable in these alloys. Wall strength is decreased at antimony contents as high as 1.0 per cent but it can be improved by the addition of pure lead.

47. (I) H. S. Phelps, A. M. Gates and F. Kahn: Internal Hydraulic Bursting Tests of Lead Cable Sheathing. *Proc.* Amer. Soc. Test. Mat. (1940) **40**, 885–903.

Although the study of creep of cable sheathing is being ably covered by H. F. Moore, it has not been definitely established whether lead of low or high creep characteristics was preferable for sheathing. However, as it is obvious that sheathing should not fail under operating pressures during the life expectancy of the cables, the most direct approach appears to be a study of the strength of cable sheathing as opposed to creep.

This paper describes a method for making reproducible hydrostatic bursting tests of cylindrical lead specimens, which has been developed to simulate service conditions. Reliable test data are now being obtained from which it is hoped to determine the kind of lead or lead alloy that will best withstand internal pressures developed in service. Results to date have revealed information about lead sheathing that gives a new conception of the problem. Suggestions are made for further study.

(II) H. F. Moore, C. W. Dollins and W. J. Craig: Bursting Tests and Tension Tests for Lead Cable Sheathing. *Proc.* Amer. Soc. Test. Mat. (1940) **40**, 904–909.

In cooperation with the Philadelphia Electric Co., comparative tests to fracture under long-time steady load were made: (1) by subjecting full sections of lead cable sheathing to internal oil pressure, and (2) by testing tension test specimens cut with the axis in a circumferential direction from pieces of the same sheathing. Four sets of tests were made, and there was found a good agreement between the nominal stress developed in the bursting tests and the tensile strength developed in the tension tests. There was also a quite good agreement between the increase of diameter in the bursting tests and the elongation of the tension-test specimens.

(III) W. H. Bassett, Jr. and C. J. Snyder: The Testing of Lead Cable Coverings. *Proc.* Amer. Soc. Test. Mat. (1940) **40**, 910–929.

A method of making long-time burst tests is described as well as the various types of physical tests that have been made on lead cable coverings in order to correlate the quality of commercial material. A new theory is suggested regarding the life of various extruded lead and lead-alloy cable sheaths subjected to constant or intermittent tensile stress. The results indicate that at some low stress, such as 400 lb. per sq. in., all types of lead and lead alloys, regardless of their tensile strength as normally expressed, will fail in approximately the same period of time.

By making four bursting tests at different pressures, the investigator can classify a given sample of lead sheath with respect to the softest lead or the hardest age-hardening alloy used by the power cable industry and can estimate its usefulness with the possible exception of resistance to corrosion and fatigue.

Joint Discussion on papers I, II, and III. Amer. Soc. Test. Mat. (1940) **40**, 930–936.

48. A. J. Phillips: Some Creep Tests on Lead and Lead Alloys. *Proc.* Amer. Soc. Test. Mat. (1936) **36**, pt. II, 170–182; discussion 183–193.

Creep-test data on lead and lead alloys from tests of three years duration are presented to show that it is unsafe to extrapolate creep rates calculated from short-time tests. Many alloying elements that increase the tensile strength of lead decrease the resistance to creep under low loads. Copper added to lead improves the creep resistance markedly. Antimony decreases the creep resistance except in the age-hardened condition where the elongation under fairly high tensile loads is practically nil. Such a metal will fracture, however, without flow under sustained loads, making it difficult, if not impossible, to calculate a safe working stress. Tin likewise decreases the creep resistance of lead, but in the heat-treated condition the alloy shows excellent creep resistance without serious loss in ductility. Tellurium added to lead decreases its creep resistance under low loads in both the hard-rolled and the annealed conditions.

49. H. J. Tapsell: The Phenomena of Creep Recovery. Int. Assn. Test. Mat. Materials Congress, London, 1937, A1-3.

The creep recovery over a given period after removal of the stress is proportional to the original applied stress, and the estimated total recovery increases with the duration of the preceding creep test. This recovery may become a relatively large fraction of both creep strain and the initial elastic strain if the initial stress is such that creep is small. Preliminary experiments indicate that the rate of recovery increases considerably with increase in temperature. The data given are a selection from numerous examples and give an idea of the extent of the creep recovery during certain tests on three steels and a lead specimen.

Nickel and Nickel Alloys

50. J. H. Bennet and D. J. McAdam Jr.: Creep Rates of Cold-drawn Nickel-copper Alloy (Monel Metal). *Jnl.* of Research, Nat. Bur. Stds. (1942) **28**, 417–437 (*Research Paper* No. 1462).

New apparatus installed in the National Bureau of Standards for tensile creep test is described. Twelve independent units for specimens having a 4-in. gauge length are provided. Temperature is controlled within ± 2.5°C. up to 650°C. and extensometer readings have a probable error of <0.00004 in. Creep tests are recorded on Monel metal samples cold-drawn to 40 per cent reduction of area, at temperatures from 370° to 663°C. The characteristic creep rate is taken as the nearly constant rate attained after an initial period of adjustment. This rate appears to be independent of previous stressing at lower or higher temperatures or stresses, and thus a single specimen was used for determining a series of characteristic creep rates at different applied stresses. Very little difference was apparent between the creep rates of annealed and cold-drawn specimens. The results are shown in a series of curves; no mathematical function could be found to describe the creep-test data.

51. C. L. Clark and A. E. White: Properties of Nonferrous Alloys at Elevated Temperatures. *Trans.* Amer. Soc. Mech. Engrs. (1931) **53**, 183.

The specimens were held at test temperature one day before loading. The load was applied in increments until creep began and was then maintained constant until creep ceased or remained constant for at least 200 hr. The load was then increased and the process repeated until at least four creep rates had been measured. Sensitivity of strain measurement, 2.8×10^{-6}.

The recrystallization temperatures of the materials were determined by hardness tests on severely cold-worked specimens before and after annealing for 5 hr. at various temperatures. The recrystallization temperature of Monel metal was found to be between 425° and 537°C. The authors place the maximum safe working temperature at 425°C. The Konel metal recrystallized between 537° and 647°C., and the author's estimate the safe working temperature as at least 537°C.

52. H. J. Tapsell and J. Bradley: Mechanical Tests at High Temperatures with Special Reference to Creep on Nonferrous Alloy of Nickel and Chromium. B.N.F.M.R.A. Report (1925) R.R.A. No. 89.

The method of tests, etc., were the same as those described under reference No. 53.

53. H. J. Tapsell and J. Bradley: Mechanical Tests at High Temperatures with Special Reference to "Creep" on a Nonferrous Alloy of Nickel and Copper (70-30). B.N.F.M.R.A. Report (1925) R.R.A. No. 94.

A number of specimens were subjected to different stresses at the temperatures considered until a stress was reached at which creep ceased after a short time. Mirror extensometers of the Marten's type were used, but the sensitivity of strain measurement was not stated. The sensitivity was, however, probably of the order of 5×10^{-5} and, since tests were conducted for periods of 56 days, it is reasonable to suppose that where specimens exhibited no perceptible creep measurements were made over a period of at least 10 days. It follows that the stresses given for no flow correspond to creep rates equal to or greater than 10^{-5} strain per day.

Tin and Tin Alloys

54. D. Hanson and W. T. Pell-Walpole: Effect of Small Additions of Tellurium on the Mechanical Properties of Pure Tin. *Jnl.* Inst. Metals (1938) **63**, 109–122.

The preparation of tin-rich tellurium-tin alloys is described. Tensile, Brinell hardness, and *creep* tests were carried out on machined chill-cast specimens and on rolled strip of alloys containing up to 0.1 per cent Te. The effect of cold-rolling and of various heat-treatment were studied.

Additions of up to 0.1 per cent Te slightly improve the Brinell hardness and tensile strength of tin, but heat-treatment of the alloys does not produce permanently improved properties. These tellurium-tin alloys have a remarkable capacity for work-hardening in the chill-cast state, but this is diminished if the ingots are annealed before deformation. Grain size may be a factor affecting work-hardening capacity. Tellurium considerably improves the creep strength of pure tin, both in the cast and in the rolled conditions. The work-hardening properties of these alloys may form a valuable guide to their relative creep strength.

Grain-size measurements were made after various mechanical and thermal treatments, and it was found that grain size has a marked effect on the creep strength of these alloys; this confirms previous work by Hanson and Sanford [*Jnl.* Inst. Metals (1938) **62**, 215] on the creep strength of other tin-rich alloys.

55. D. Hanson and E. J. Sanford: The Creep of Tin and Tin Alloys, Pt. I. *Jnl.* Inst. Metals (1936) **59**, 159–176; discussion

176–178, correspondence 177–178, Pt. II, (1938) **62,** 215–233; discussion, 234–236, correspondence, 236–237.

Pt. I. The paper describes results of creep tests of long duration on tin and some of its alloys in the rolled condition. Silver up to 3.5 per cent greatly improves the creep resistance of tin. Bismuth-tin alloys are more resistant to flow than pure tin at stresses above about 300 lb. per sq. in., but at lower stresses they are inferior to pure tin. Antimony improves the creep properties of tin: the alloy containing 8.5 per cent Sb withstands a stress three times that of pure tin for an equal duration. Cadmium-tin alloys are greatly improved by heat-treatment and offer considerable resistance to creep. The mechanism of failure of these alloys is discussed. Results are given of tests on lead-tin solders and on the cadmium-tin eutectic alloy: these flow under stresses as low as 130–150 lb. per sq. in. It is shown that in many cases there is no relationship between resistance to creep and ultimate tensile strength.

Pt. II. A description is given of results of creep tests on alloys of tin with 2 to 7 per cent Cd and 3 to 9 per cent Sb. The influence of annealing at 170° and at 200°C. is discussed. After cold-rolling and self-annealing, the best alloy is that containing 7 per cent Cd and 9 per cent Sb; it withstands a stress of 1200 to 1400 lb. per sq. in. for many years. After annealing at 170°C., the most beneficial composition is 2 per cent Cd and 7 per cent Sb; a safe stress for this alloy is 3500 lb. per sq. in. Annealing at 200°C. produces optimum creep properties at a composition of 3 per cent Cd and 7 per cent Sb; a safe stress in this case is 3700 lb. per sq. in. It is shown that grain size is an important factor in determining creep-resistance; therefore, as the tensile strength is not greatly influenced by grain size, no relationship is found between these two properties in the annealed alloys investigated. The effect of additions of 1 and 2 per cent Ag, 1 per cent Cu, or 0.3 per cent is discussed. The silver and copper alloys show similar creep properties, but the nickel alloy is inferior. An alloy containing 1 per cent Cd and 3.5 per cent Ag has great creep resistance when cold-rolled and self-annealed; it is superior to the alloy containing 7 per cent Cd and 9 per cent Sb.

Zinc and Zinc Alloys

56. C. Haase and H. Wurst: Mechanical Properties and Corrosion Behavior of High-zinc Alloys, with reference to their use as electrical conductors. *Ztsch. Metallkunde* (1942) **34,** 81–85.

Zinc containing 1 per cent aluminum or copper has been used for making electrical conductors in Germany, but frequent troubles have occurred because the wires have become brittle. This brittleness appears to be due largely to the percentage of alloying element and the amount of impurities present, and to the texture; it occurs with finer grain sizes the greater is the amount of second phase present. Coarse grain growth by recrystallization on annealing is not a determining factor if impurities are absent. Annealing at a low temperature (e.g., 150°C.) considerably reduces the tendency to embrittlement, as also does the addition of 0.2 per cent of manganese. This addition improves the resistance to creep and corrosion without appreciably affecting the workability of the mechanical properties.

57. W. Jung-Koenig, E. Schmid and H. D. Graf v. Schweinitz: Adaptation of Hardness-time Curves for the Evaluation of Creep Relationships. *Metallwirtschaft* (1940) **19,** 492–494.

A short simple procedure is described, which allows a quantitative comparison of the creep resistance of different materials in the recrystallization region. Data are presented in graphical form for pure zinc and two zinc alloys containing (1) aluminum 10, copper 0.3 per cent, and (2) aluminum 10, copper 0.5, magnesium 0.03 per cent. Brinell hardness, measured on a modified Rockwell-type machine, is plotted against time of loading at loads from 12.7 to 1.6 kg. per sq. mm. Maximum hardness for all times of loading occurs at a load of about 12.7 kg. per sq. mm. An exact quantitative evaluation of the curves has not been carried out, but a rough numerical index of creep resistance may be used, based on the mean speed of penetration during a total time of loading of 20 minutes, which gives values ranging from 25.5 × 10^{-4} in the case of pure zinc to 4.5 × 10^{-4} (minute in the case of alloy b).

58. K. Loehberg: Creep Behavior of Technical Zinc Alloys. *Metallwirtschaft,* (1941) **20,** 825–831.

Tests made on zinc-aluminum and zinc-aluminum-copper alloys at 20° and 100°C. show that the relative resistance to creep can be determined by plotting the depths of penetration of a steel ball under various loads against the time of application of the load. The resultant "hardness-creep" curves have a shape similar to the usual rate of elongation-load curves. The creep limit of sand-cast 95-4-1 zinc-aluminum-copper alloy is slightly better than that of the extruded alloy and very much better than that of the 90-10 zinc-aluminum alloy. Drawing of the ternary alloy greatly reduces the resistance to creep, but subsequent aging at 150°C. partly, and aging at 300°C. almost completely, restores the original value. Similar effects are shown by the 89-10-1 zinc-aluminum-copper alloy. With both these alloys the resistance to creep both at 20° and at 100°C. decreases linearly with increasing degree of reduction by drawing; even after 60 per cent reduction the original value of the creep resistance is restored by aging at 300°C. for 5 days.

59. K. Loehberg and F. Wolbank: Hardness-creep Experiments on Zinc Alloys. *Ztsch. Metallkunde* (1940) **32,** 419–424.

The penetration of a 2.5-mm. ball under a constant load of 31.25 kg. was measured as a function of the time in minutes over a period of 20 min. The composition of the zinc alloys used varied from 1.7 per cent Al, 0 per cent Cu and 98.3 per cent Zn to

0 per cent Al, 2.5 Cu and 97.5 Zn. In general, the depth of penetration decreased to a minimum corresponding to the maximum solid solubility. A definite interrelation existed between the phase diagram and the creep behavior. Small additions of magnesium (up to 0.02 per cent) improved the creep strength. A suitable heat-treatment eliminated the harmful effect of cold-work deformation on the rate of penetration and the final depth of penetration (after 20 minutes).

Design

60. R. W. Bailey: Design Aspect of Creep. *Jnl. Applied Mechanics* (A.S.M.E.) (1936) **3**, A1–6.

    Some of the more important factors concerned in the development of a rational treatment of creep for the purpose of engineering design are briefly dealt with, and consideration is given to the applications of creep to design problems with particular reference to hollow cylinders subjected to internal pressure, steam piping and rotating disks. The determination of creep properties for design as regards permissible stresses, relation between creep rates, and the influence of prolonged heating on creep properties are also dealt with, and it is stated that in spite of the complicated nature of creep phenomena there is no reason why the treatment of creep design should not be as satisfactory and reliable as the treatment used for materials under elastic conditions.
61. R. W. Bailey: Utilization of Creep Test Data in Engineering Design (Creep of Lead Tubes under Compound Stress). *Proc.* Inst. Mech. Engrs. (1935) **131**, 131–269; discussion, 269–349.

    The purpose of the paper is to outline a rational treatment of the subject of creep, particularly directed to the requirements of design. Experimental data are examined and general expressions for creep under any system of stress are given, which include the case of tension, and permit the results of tensile creep tests to be utilized in the design of parts under complex stress. General relationships are suggested for creep in the direction of three principal stresses X, Y, and Z (considered positive when tensile) representing any stress system. The expressions are similar in form; e.g., the tensile creep rate C_x in the direction of X is represented by

    $$C_x = \frac{A}{2}\left[\frac{1}{2}(X - Y)^2 \frac{1}{2}(Z - X)^2 \frac{1}{2}(Y - Z)^2\right]^m \\ [(X - Y)^{n-2m} - (Z - X)^{n-2m}]$$

    where A, m and n are constants. For simple tension ($Y = 0$, $Z = 0$) $C_x = AX^n$. Values of m and n are derived. The distribution of stress in important engineering parts under compound stress is determined, including tubes, pipes, cylinders (with and without heat transmission) under internal pressure, bending moment and torque, and also the stress distribution in rotating discs and rotors. The paper also includes results for the axial, circumferential (twist) and diametral creep of lead pipes under combined internal pressure and axial stress, and internal pressure and axial torsion; data for steel tubes under compound stress are also given.
62. E. A. Davis: High-temperature Design. *Product Engineering* (March 1939) **10**, 104–106.

    How to interpret and apply creep data in designing member for high-temperature service, interpreting creep curves, selecting design stresses, calculating deformation; sources for creep data.

DISCUSSION

(*H. L. Burghoff presiding*)

A. I. Blank.*—Mr. Kanter has spoken of failures from causes other than creep itself in metals that are subjected to creep stresses. Would it be possible for the author to enlarge on this very important matter of "cataclysmic types of failures?"

J. J. Kanter.—Of course, it is always a delicate matter to discuss specific failures. I would prefer to keep the present discussion on fundamentals and principles.

H. L. Burghoff.*—Mr. Kanter, I should like to ask what you consider the responsibility of the designer in avoiding stress concentrations that would lead to these types of failures?

J. J. Kanter.—It was my feeling in looking over the papers of this symposium that they were significantly lacking in consideration of what happens to the metals when strained under conditions that lead to rupture. Often creep tests are run that produce only a fractional percentage of the deformation, in several thousand hours. That kind of information gives the designer no assurance whatever that cracks will not result in his structure at points where stress concentrations, and therefore deformation concentrations, exist. I think anyone in this day and age who presents a paper on creep should incorporate with those studies a thorough investigation of creep rupture if it is expected to make an impression upon the design engineer.

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* Chase Brass and Copper Co., Waterbury, Connecticut.

H. L. EISELSTEIN.*—Since most creep tests are made in direct tension, what methods do you use for design of the combined stress, such as combined portion or tension or compression?

J. J. KANTER.—The combined-stress problem is a very difficult one experimentally, but some work has been done upon it. Perhaps the combined-stress problem is best met by making some kind of operating test upon the actual structure wherever possible. For pressure vessels, tests of that kind are generally resorted to and considerable information exists.

It is indeed an extremely difficult matter experimentally to try to meet the combined-stress problem, and I thoroughly agree with you that investigations under simple tension do not reflect the conditions for failure. I would say that a material that shows excellent stress-rupture properties, though, is much better capable of standing abuses under combined stress than one that does not show good stress-rupture properties. There are certain aspects of the stress-rupture condition that will show up inherent weaknesses that come to light under combined stress.

E. E. SCHUMACHER.†—There has been some effort in recent years to devise a rapid test procedure for determining creep. Since it is impossible to accelerate time, it has been my feeling that the chances for finding such a test were poor. I should like to have your opinion on this subject.

J. J. KANTER.—I do not think that it is so vitally necessary to work out a rapid test for creep. There is a great volume of information accumulating on most basic materials, which gives the designer a fairly reliable gauge of what order of stress can be applied to a structure. What he needs to know in most cases, more than creep stress, is whether the material can be depended upon to stay good for the life of the structure.

F. G. TATNALL.‡—I desire to pursue this matter of cataclysmic failure. I do not know where to find a description of cataclysmic failure, and so I ask Mr. Kanter.

J. J. KANTER.—Under the term cataclysmic failure, I am summarizing all failures that are accompanied by an extensive amount of damage engendering doubt in the minds of engineers regarding all similar structures. I have in mind one such failure, which took place in a certain power plant about a year and a half ago, where everything had been correctly designed from the creep standpoint but the vital matter of the stability of materials had been overlooked. There was a considerable amount of damage done to both equipment and engineering prestige that I am inclined to exemplify as cataclysmic. Incidentally, that particular incident has opened the eyes of many metallurgists as to what they really ought to be concerned about in high-temperature structures in addition to creep.

A. J. SMITH.*—Mr. Kanter has been rather easy on the designing engineers, in that the design engineer works very largely on empirical formulas and takes into account what he calls a "factor of safety." An engineering textbook a good many years ago said that the term would better be called a "factor of ignorance."

Consider a part like that Mr. Kanter is making and that we are making in the form of a valve body. I am not sure that the design engineer knows exactly what the stresses are in that valve body, particularly with the high pressure and high temperature involved. We do not know what a workman will do after the valve is in service—whether he will turn the wheel with his hand or put a pipe wrench on it to get it tight, nor does the design engineer know exactly, when he is designing that valve, what the workman is going to use when he closes it.

In reference to the failure that Mr. Kanter cited, where there was concomitant failure in another part of the system, perhaps we could say what the stresses were on that pipe-line cutout, but because of the other failure we do not know what the stresses were that were applied as a result. Had they been just the normal stresses, the failure might not have occurred. Perhaps the failure was so bad it was bound to happen in a short while anyway. Here in this one instance it is very possible the failure was accelerated by the other failure that had just occurred.

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† Bell Telephone Laboratories, Murray Hill, New Jersey.

‡ Baldwin Locomotive Works, Eddystone, Pennsylvania.

* Lunkenheimer Company, Cincinnati, Ohio.

That is something the design engineer cannot quite take into account. The only thing, it seems, that will provide an answer, is the actual measurement of the stress in the part under the most severe loading that can be made. Fortunately, we are developing today, and it has been discussed before at A.I.M.E. meetings, a strain gauge that can be set on the location in question to find out at least what the strains are; and if our interpretations are any good, perhaps we can find out something about the stresses in that same location—and I believe the stresses will be found to be very different from what we figure as nominal design stresses to which we apply this factor of safety.

J. J. KANTER.—In addition to Mr. Smith's timely remarks, I should like to submit the fact that in valve bodies and similar devices I have never yet seen an actual failure that could be attributed to creep. True, the stress design engineer has not taken into consideration many factors he might have considered, but the peculiar fact of the situation is that creep stress has been given abundant attention and it is other factors to which stricter attention must yet be paid. Frequently, overstressing of a structure may be due to transient thermal gradients or "heat shocks," which bring into play properties of the materials that are not reflected in long-time creep or rupture tests. I think that while the design engineer may be at fault, he frequently needs information on some of these other properties for which none is obtained, from creep investigations in the manner they are conducted or reported.

H. F. MCCULLOUGH.*—In the category of the type of stresses that Mr. Kanter talked about, we have had failures, as all of you probably have had. They have been serious failures that involved a lot of money. In this particular case, it was failure of electrical conductors in rotating machinery. The type of failure that occurred did not show much deformation of the rotor conductor in the vicinity of the failures but it did show intergranular cracking set up by long-time temperature and stress.

J. J. KANTER.—Yes, the type of failure that Mr. McCullough speaks of is perhaps typical of the way in which many nonferrous metals have ruptured, where failures have occurred. It is for this reason that so much emphasis is placed upon making stress-rupture tests. Such testing frequently reveals susceptibility to intergranular cracking, where conventional creep testing conveys no indication.

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* General Electric Co., Schenectady, New York.

Creep Characteristics of a Phosphorized Copper

By H. L. Burghoff,* Member, and A. I. Blank,† Junior Member, A.I.M.E.

(Cleveland Meeting, October 1944)

The state of knowledge bearing on the stability of copper under stress at elevated temperatures is generally known to be in need of revision and extension. The present investigation, dealing with the creep characteristics of a deoxidized copper of low residual phosphorus content, is intended to contribute in some small measure toward this end. The experimental data presented herein have been correlated by methods of evaluation and interpretation familiar to those who are concerned with creep of metals.

In practice it is common, if not requisite, to use structurally stable materials at elevated temperatures. It is frequently desirable, however, to test materials under conditions that produce structural change, in order to determine the extent of such change and its effect on physical properties, thus making it possible to establish accurately the limiting conditions to which such materials may be safely exposed. The creep characteristics of the drawn copper wire of this investigation are directly associated with its structural instability at elevated temperatures. Complete realization of this fact is essential to the evaluation of its creep resistance under various conditions.

Creep results should apply to steady deformation under equilibrium conditions, but these are seldom attained in only one or two thousand hours. It will be shown that steady creep rate for copper at useful stresses does not usually begin until considerably more time has elapsed. A wholly satisfactory substitute or shortcut for extensive creep testing does not appear to be evident in the application of mathematical analyses to limited experimental data.

Material

A single lot of phosphorized copper wire was drawn down to 0.125-in. diameter with a final reduction of 84 per cent. After mechanical straightening, a portion of this wire was annealed to an average grain size of 0.013 mm. in a controlled-atmosphere furnace. The composition and initial properties of the copper in these two conditions are listed in Table 1. Photomicrographs of the original structure are shown in Fig. 1.

Table 1.—*Composition and Initial Properties*

	Cu	P	Fe	Ni
Composition, per cent	99.95	0.008	0.001	0.001

	Drawn 84 Per Cent	Annealed 0.013 Mm.
Modulus of elasticity, lb. per sq. in.	19,000,000	
Stress at 0.2 per cent offset, lb. per sq. in.	53,000	
Yield strength at 0.5 per cent extension, lb. per sq. in.	54,000	12,000
Tensile strength, lb. per sq. in.	57,500	36,500
Elongation in 2 in., per cent	8.0	48.0
Electrical conductivity, per cent I.A.C.S.	98.3	100.1

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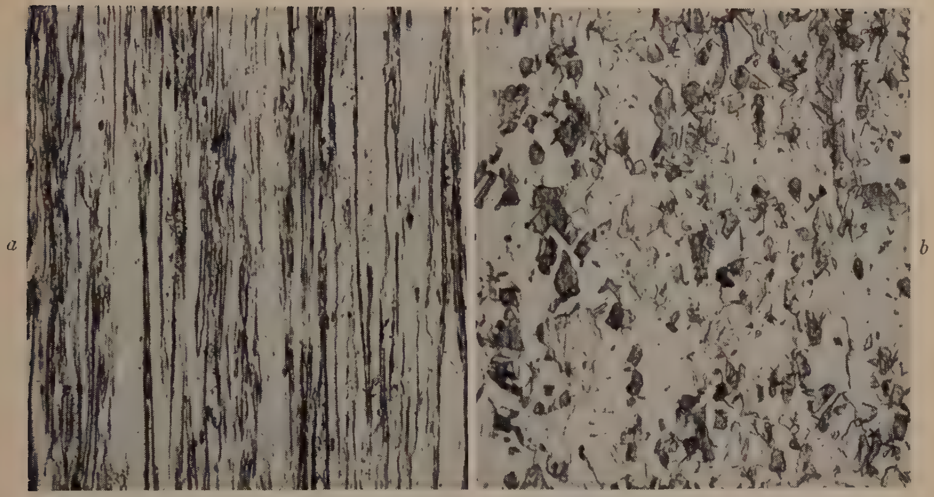

FIG. 1.—MICROSTRUCTURE OF PHOSPHORIZED COPPER WIRE. × 250. *a*, as drawn 84 per cent. *b*, as annealed, 0.013 mm. Average grain size.

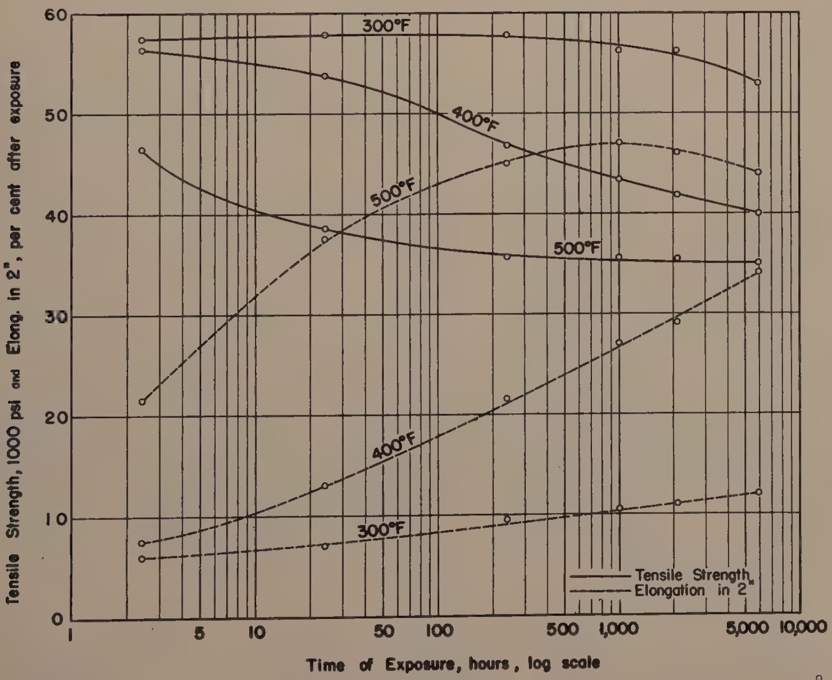

FIG. 2.—TENSILE CHARACTERISTICS OF DRAWN MATERIAL AS FUNCTIONS OF TIME AT 300°, 400°, AND 500°F.

Tensile strength and elongation in the processed condition are 57,500 lb. per sq. in. and 8.0 per cent in 2 in., respectively.

EXPERIMENTAL PROCEDURE

Tension creep tests were made at 300°, 400° and 500°F. The 0.125-in. diameter wire specimens were mounted vertically in electrically heated, forced convection furnaces. Time variation of temperature was held to within 2°F. by automatic controls and the temperature distribution over the 10-in. gauge length did not exceed 5°F. Extension was measured optically by means of a system of markings on blocks attached to each specimen and to a reference wire of the same material. The method compensated automatically for thermal expansion. Sensitivity of measurement of extension was 0.001 per cent. The equipment and test procedure have been previously described in greater detail.[1]

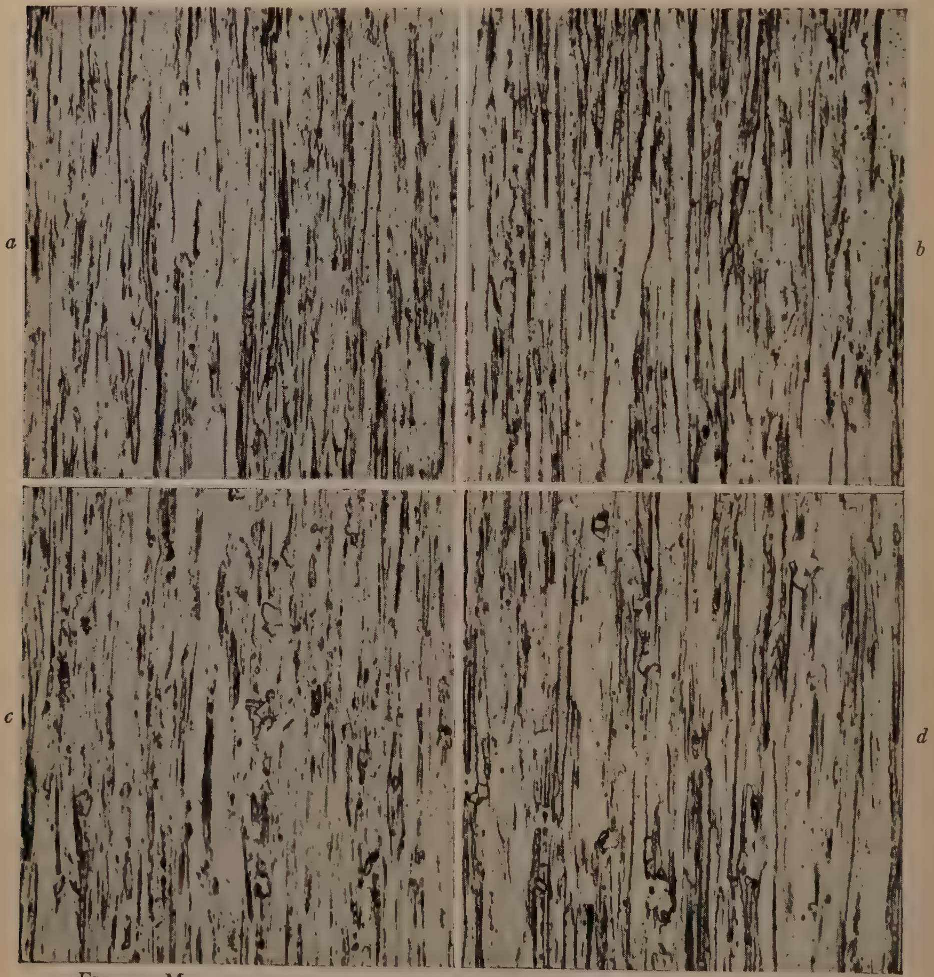

FIG. 3.—MICROSTRUCTURE OF DRAWN WIRE AFTER EXPOSURE AT 300°F. × 250.
a, 2.4 hours; *b*, 240 hours; *c*, 1000 hours; *d*, 5900 hours.

Inasmuch as recrystallization occurred to various degrees in the hard-drawn wire during the course of the exposures at each of the three testing temperatures, a series of tests was made to determine the effect of time of exposure upon structure and ordinary tensile properties. The specimens for these experiments were unstressed wires and periods of exposure ranged from 2.4 to 5900 hours.

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[1] References are at the end of the paper.

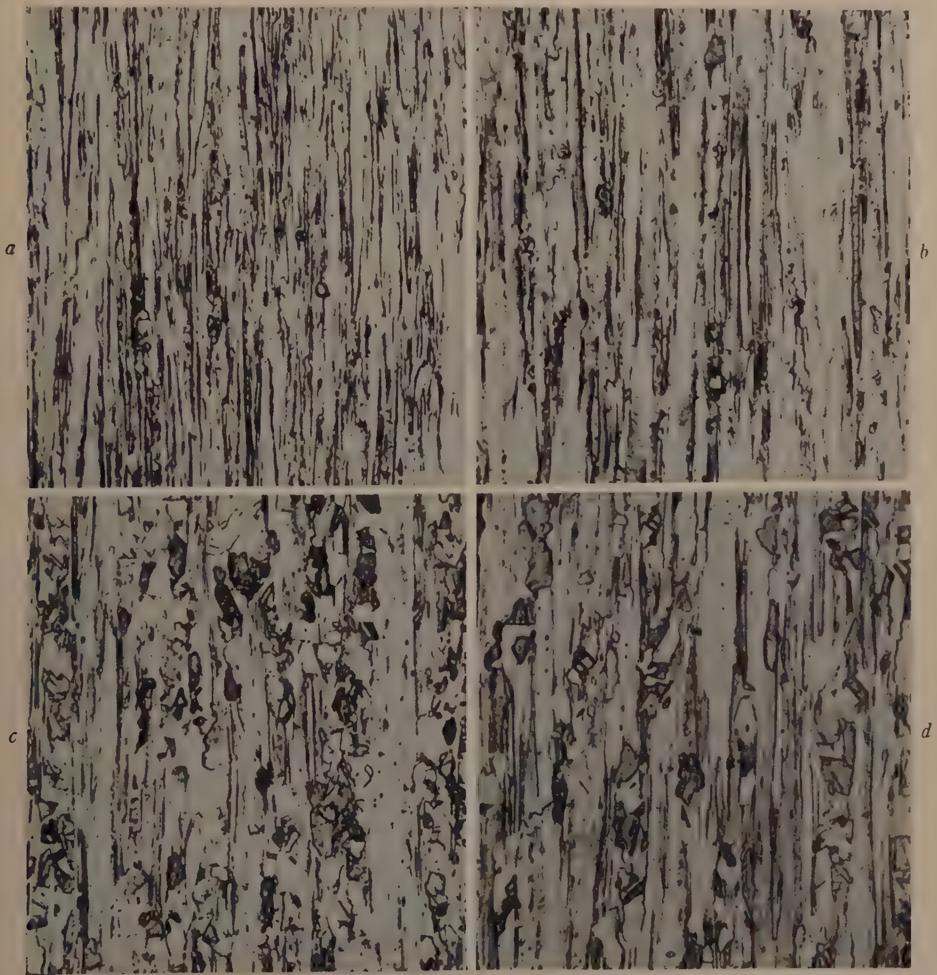

Fig. 4.—Microstructures of drawn wire after exposures at 400°F. × 250.
a, 2.4 hours; *b*, 24 hours; *c*, 240 hours; *d*, 1000 hours.

Structural Stability

Structural stability of both the drawn copper and the annealed copper was determined by measurement of tensile properties and examination of microstructure at room temperature after exposure in the creep tests. Enough of these data are listed in Table 2 to show the marked stability of the annealed temper and the lack of stability of the drawn temper at all three temperatures. The changes in tensile properties of the annealed temper are of negligible magnitude. The variations in the elongation values for the annealed material listed in Table 2 are the result

TABLE 2.—*Room-temperature Properties before and after Creep Tests*

Creep Testing			Yield Strength, (0.5 Per Cent Elongation) Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent	Microstructure
Temperature, Deg. F.	Stress, Lb. per Sq. In.	Time, Hr.				
			Annealed 0.013 Millimeter			
			12,000[a]	36,500[a]	48[a]	Annealed
300	6,450	6,050		36,500	43	Unchanged
300	0	6,050		35,800	48	Unchanged
300	8,450	5,300		38,300	37	Unchanged
300	0	5,300		37,800	42	Unchanged
400	2,050	6,600		35,900	44	Unchanged
400	0	6,600		35,800	46	Unchanged
400	5,100	6,600		36,100	46	Unchanged
400	0	6,600		36,000	47	Unchanged
500	1,000	5,000		35,200	44	Unchanged
500	0	5,000		34,900	44	Unchanged
500	2,000	5,000		34,700	42	Unchanged
500	0	5,000		35,000	46	Unchanged
			Drawn 84 Per Cent			
			54,000[a]	57,500[a]	8[a]	Hard-drawn
300	10,400	5,280		52,000	10	Very slightly recrystallized
300	0	5,280		53,000	12	Very slightly recrystallized
300	25,800	5,400		52,200	14	Very slightly recrystallized
300	0	5,400		52,900	12	Very slightly recrystallized
400	3,050	5,200		39,100	34	Recrystallization well advanced
400	0	5,200		38,900	36	Recrystallization well advanced
400	8,100	5,300		39,700	34	Recrystallization well advanced
400	0	5,300		39,900	34	Recrystallization well advanced
500	1,000	5,550		35,000	45	Completely recrystallized
500	0	5,550		35,000	46	Completely recrystallized
500	2,050	6,350		34,500	45	Completely recrystallized
500	0	6,350		34,700	45	Completely recrystallized

[a] Before creep tests.

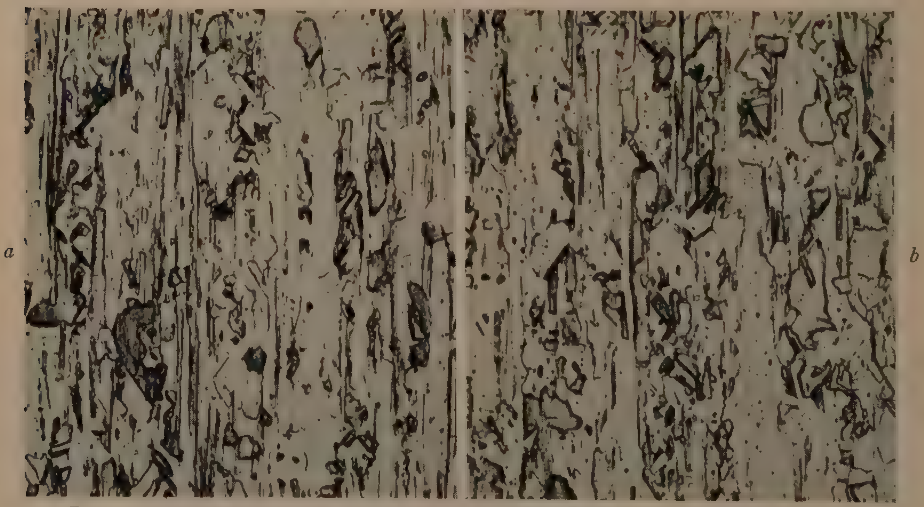

FIG. 5.—MICROSTRUCTURES OF DRAWN WIRE AFTER EXPOSURES AT 400°F. × 250.
a, 2100 hours; *b*, 5900 hours.

of the unavoidable use of short tensile specimens that fractured close to the gauge marks and grips in many instances. With the drawn temper, there is an appreciable loss of tensile strength even at 300°F. At higher temperatures there is much greater loss of tensile strength, as shown by the data. Decrease in tensile strength is accompanied by normal increase in elongation. These changes in tensile properties of the drawn temper are indicative of the same order of softening that is to be expected from the degree of recrystallization evident in the microstructures after exposure. The structure of the annealed temper, on the other hand, seems perfectly stable because it is in no way affected by any of the exposures.

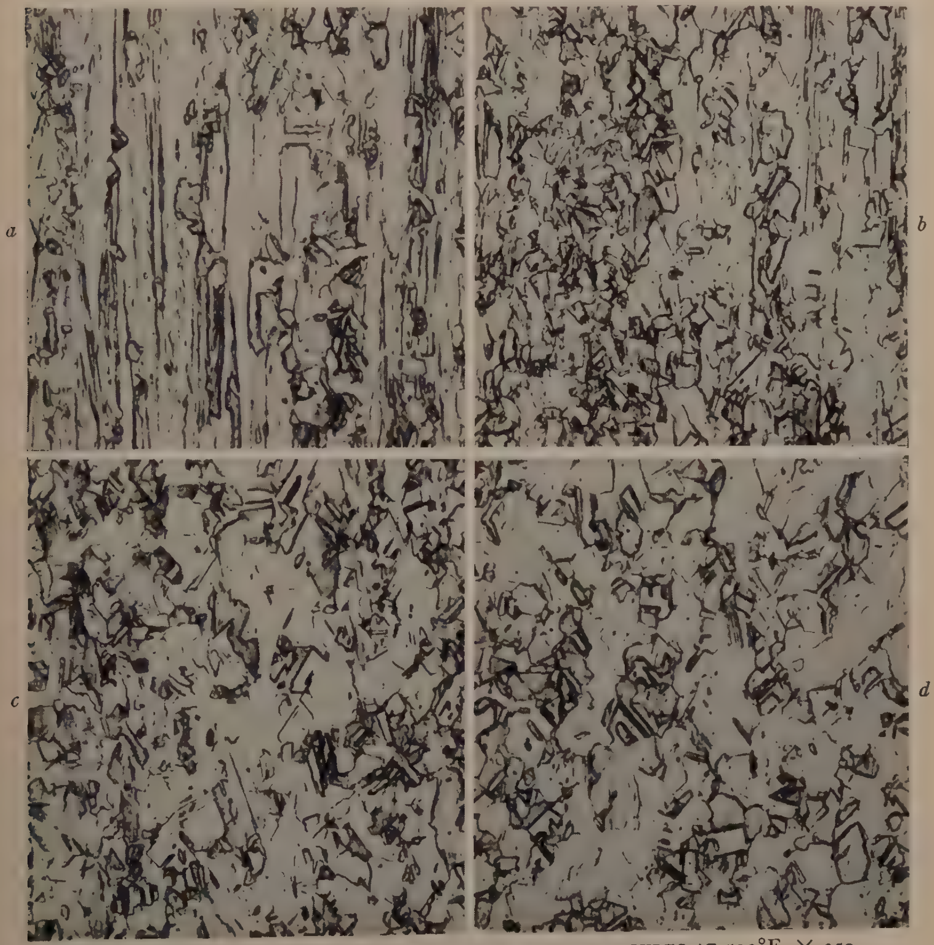

FIG. 6.—MICROSTRUCTURES OF DRAWN WIRE AFTER EXPOSURES AT 500°F. × 250.
a, 2.4 hours; *b*, 24 hours; *c*, 240 hours; *d*, 5900 hours.

Since creep characteristics are greatly dependent on structure, it is obvious that the extent of structural transformation of the drawn wire warrants consideration in an appraisal of its creep properties. The study of this severely drawn material as exposed at the three temperatures for periods of time ranging from 2.4 to 5900 hr.

yielded considerable information concerning its softening and recrystallization characteristics. Tensile strength and elongation, measured at room temperature after each exposure, are shown graphically in Fig. 2, and most of the corresponding structures are shown in the photomicrographs of Figs. 3 to 6.

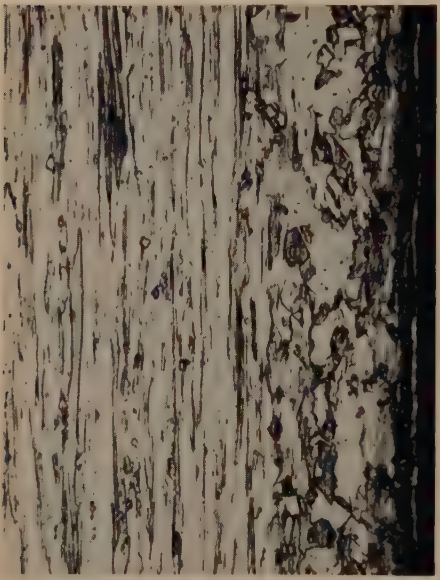

FIG. 7.—MICROSTRUCTURE AT EDGE OF DRAWN WIRE AFTER EXPOSURE FOR 1000 HOURS AT 300°F. × 250.

At 300°F. the tensile strength remains essentially unchanged until almost 500 hr. has elapsed, and then it begins to decrease slowly. Confirmation of this variation with time is found in the corresponding photomicrographs of Fig. 3. Exposures approaching 1000 hr. at 300°F. are necessary in order to develop the first visible evidence of recrystallization, which does not increase materially even after 5900 hr. In a very thin region at the surface of the wire, some recrystallization is evident after 240 hr. and is unquestionably associated with the working of the surface layers of the wire in the straightening operation. This latter, preferential recrystallization, illustrated by Fig. 7, occurs at 400°F. also, but it is of no great consequence, since it develops only in a comparatively small portion of the cross section of the wire.

At 400°F. the tensile strength falls off more rapidly than at 300°F. and reaches a much lower value after 5900 hr. at temperature. The rate of change of tensile strength is quite rapid during the first 100 hr. at 400°F. but decreases thereafter as the tensile strength approaches a final, annealed value. At this temperature, recrystallization is just perceptible at 2.4 hr., extends through approximately 40 per cent of the structure at 240 hr., and thereafter proceeds at a diminishing rate. After 5900 hr., recrystallization seems somewhat more than half complete. Tensile strength changes are in accordance with the progress of recrystallization.

At 500°F. the tensile strength falls off sharply during the first few hours and then proceeds at a decreasing rate toward a final value for annealed material. The very short time necessary to effect complete recrystallization at this temperature is apparent in Fig. 6. Recrystallization is perhaps 30 per cent complete at 2.4 hr., almost complete at 24 hr., and entirely complete at 240 hours.

Elongation increases with time in somewhat the same manner as the tensile strength decreases. Applying these results to the creep tests, it is evident that the original temper of the drawn copper is retained during an appreciable part of the testing time only at 300°F., and at the two higher temperatures there is practically no structural stability. Thus, in conducting the creep tests on this severely drawn material at 300°, 400° and 500°F., three materials really are involved: (1) at 300°F., one essentially as cold-worked; (2) at 400°F., one containing substantial proportions of both cold-worked and annealed grains; (3) at 500°F., one essentially in the fully recrystallized condition.

DISCUSSION OF CREEP TEST RESULTS

The creep or time-extension curves for all of the tests are shown in Figs. 8 to 13. These curves show total extension, which includes the initial extension occurring upon application of load at zero time, and the subsequent creep. The smooth curves drawn through the experimental points form the basis of all subsequent analysis of the test results. Creep rates at various stages were determined from these primary curves as replotted on scales sufficiently open to permit accurate measurement of slope. The ordinate scales in Figs. 8 to 13 were contracted for convenience in reproduction.

Numerical creep test data are shown in Table 3. The creep intercept, e_0, and final creep rate, v, were derived from the creep curves and are for application in the McVetty type of formula:[2]

$$\text{Creep} = e_0 + vt$$

where e_0 = a constant (intercept for 0 time on creep-time plot),

v = creep rate (slope or tangent to creep curve), and

t = time.

With some exception, the creep rate listed is that in effect at the end of the test. The exceptions are for three creep curves that had entered the third stage, that of acceler-

TABLE 3.—*Results of Creep Tests*

Testing Temperature, Deg. F.	Stress, Lb. per Sq. In.	Total Time, Hr.	Initial Extension, Per Cent	Total Creep, Per Cent	Creep Intercept (e_0), Per Cent	Final Creep Rate v, Per Cent per 1000 Hr.	Stress for Designated Creep Rate, Lb. per Sq. In.		
							0.001 Per Cent per 1000 Hr.	0.01 Per Cent per 1000 Hr.	0.1 Per Cent per 1000 Hr.
Temper: Annealed 0.013 Millimeter									
300	2,100	5,900	0.008	0.018	0.015	0.0005	2,900	7,200	9,500
	6,450	6,050	0.040	0.086	0.041	0.0074			
	7,750	5,050	0.052	0.150	0.093	0.011			
	8,450	5,300	0.060	0.348	0.187	0.030			
	10,400	900	0.81	1.30	1.180	0.135[a]			
400	1,000	5,400	0.004	0.022	0.006	0.0030	500	2,100	5,400
	2,050	6,600	0.007	0.121	0.047	0.011			
	3,600	5,400	0.020	0.230	0.083	0.027			
	5,100	6,600	0.042	1.440	0.786	0.10			
	7,300	2,350	0.115	1.935	1.320	0.26			
500	500	6,600	0.003	0.036	0.006	0.0047		700	1,950
	1,000	5,000	0.005	0.175	0.054	0.024			
	2,000	5,000	0.010	0.660	0.150	0.10			
	3,100	5,750	0.018	2.310	0.602	0.30			
Temper: Drawn 84 Per Cent									
300	7,250	5,350	0.035	0.018	0.014	0.0008	8,000	21,000	
	10,400	5,280	0.043	0.037	0.027	0.0019			
	17,550	5,900	0.095	0.063	0.028	0.0060			
	25,800	5,400	0.155	0.183	0.077	0.020			
	30,900	5,280	0.187	0.432	0.072	0.050[a]			
400	1,000	5,200	0.005	0.022	0.015	0.0014	500[b]	5,200	
	2,050	5,400	0.013	0.038	0.026	0.0023			
	3,050	5,200	0.020	0.054	0.035	0.0036			
	5,100	5,400	0.033	0.112	0.050	0.011			
	8,100	5,300	0.052	0.282	0.075	0.037[a]			
500	500	5,300	0.005	0.052	0.014	0.0071		600	2,300
	1,000	5,550	0.011	0.140	0.029	0.020			
	2,050	6,350	0.022	0.610	0.033	0.091			
	3,050	6,600	0.032	1.580	0.246	0.20			

[a] Minimum rate before third stage of creep.
[b] By extrapolation.

ating rate, and in these cases the rates given are the minimum rates developed before the incidence of the third stage.

Data from Table 3 were used in the construction of Fig. 14, which shows the relationships between stress and creep rate as plotted on logarithmic scales. These curves illustrate the relative creep resistance of the drawn and annealed tempers at each of the three testing temperatures. The creep resistance of the drawn temper is approximately three times that of the annealed temper over most of the range covered by the curves at 300°F. The curves for the two tempers at 400°F. are somewhat less evenly displaced from each other than are those at 300°F. and the relative superiority of the drawn temper is somewhat diminished at this higher temperature. The creep strength ratio favoring the drawn temper varies between 2 and 2.6 over most of the range at 400°F. At 500°F., both tempers have nearly equal creep properties. From the point of view of

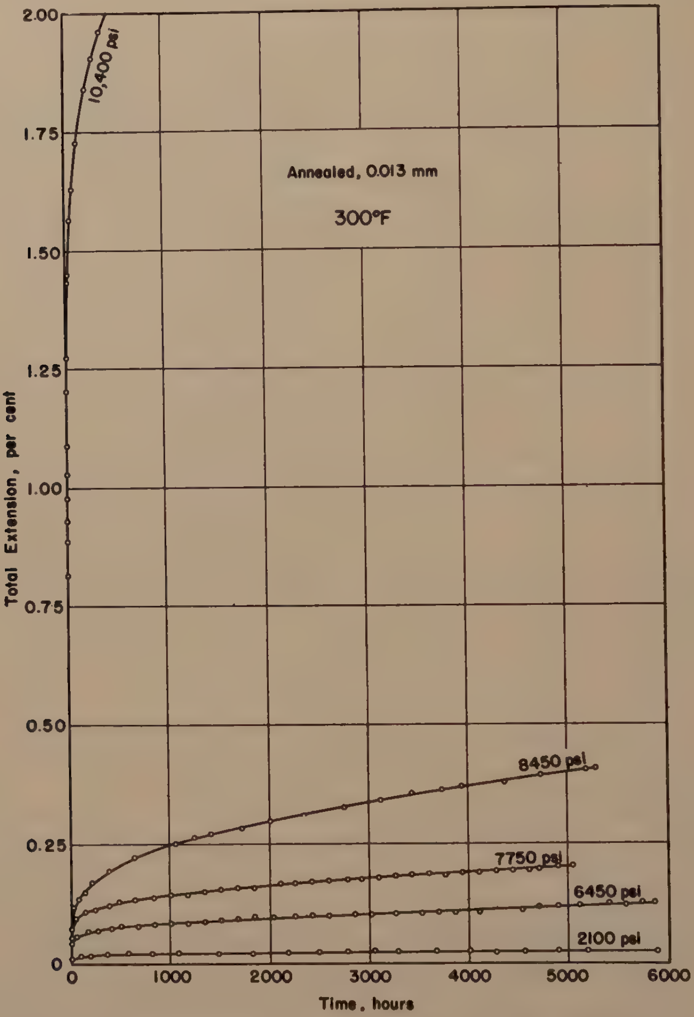

FIG. 8.—TIME-EXTENSION CURVES AT 300°F. FOR ANNEALED TEMPER.

stress, the curves at this temperature are nowhere separated by more than 500 lb. per sq. inch.

The hyperbolic sine method of analysis described by Nadai[3] and McVetty[4] was applied to pairs of points on the curves for log stress vs. log creep rate of Fig. 14. In some instances there was fairly close agreement between the remaining experimental data and the calculated curves that were obtained according to this method. The fact that a true, steady creep rate was attained in less than half of the tests might at this point be considered to explain why some of the data failed to conform satisfactorily with the mathematical analysis. In addition, it is believed that variations in the creep mechanism over a range of temperatures and stresses are so numerous and complex that a single function is not adequate to form a basis for extrapolation of the stress-creep rate relationship for all materials. Factors supporting this contention have been ably pointed out by Gillett.[5]

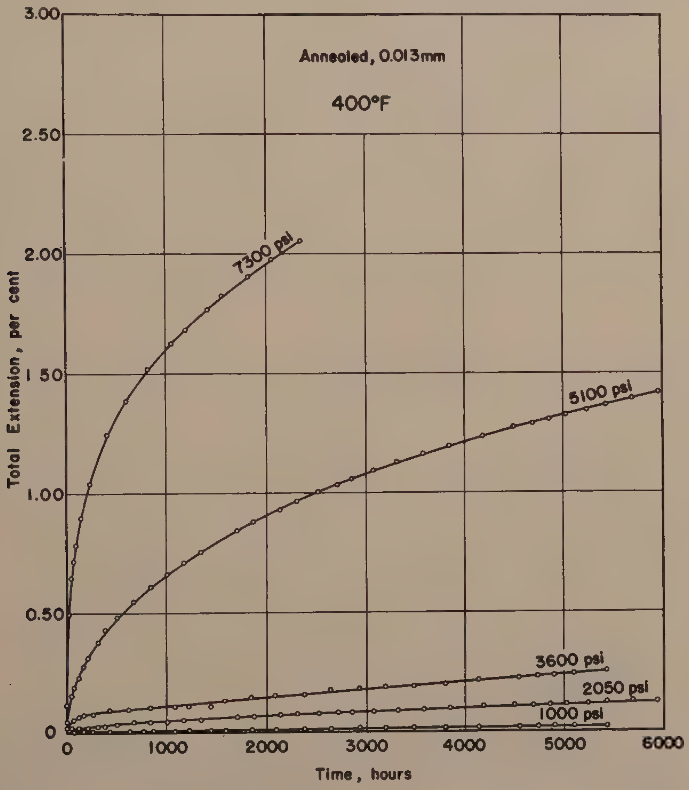

FIG. 9.—TIME-EXTENSION CURVES AT 400°F. FOR ANNEALED TEMPER.

Since the parabolic power function[6] relating stress and creep rate gives a straight line on the logarithmic plot, it fails generally to describe the curves of Fig. 14. Only the curve of the annealed material at 500°F. can be drawn as a straight line. The remaining four curves are perhaps more nearly described by the hyperbolic sine function, at least over limited ranges of stress.

The stress-creep rate curve for the drawn material at 400°F. in Fig. 14 is a striking illustration of the inconsistencies of the creep process. The marked change in slope of this curve near 3000 lb. per sq. in. seems to indicate that the factors influencing the creep process may be somewhat different above and below a critical stress. The curve might perhaps be satisfied by two hyperbolic sine equations but not by one alone. Extrapolation based on an equation satisfying the portion of the curve above 3000 lb. per sq. in. indicates considerably lower creep rates for stresses below 3000 lb. per sq. in. than were actually found. The type of relationship between stress and rate of deformation by shear where there is a definite change in slope of the curve at a critical stress has been analyzed by Gemant,[7] who claims that the early portion of the curves is linear, indicating constant viscosity, and that the later portion, involving changing viscosity, is logarithmic.

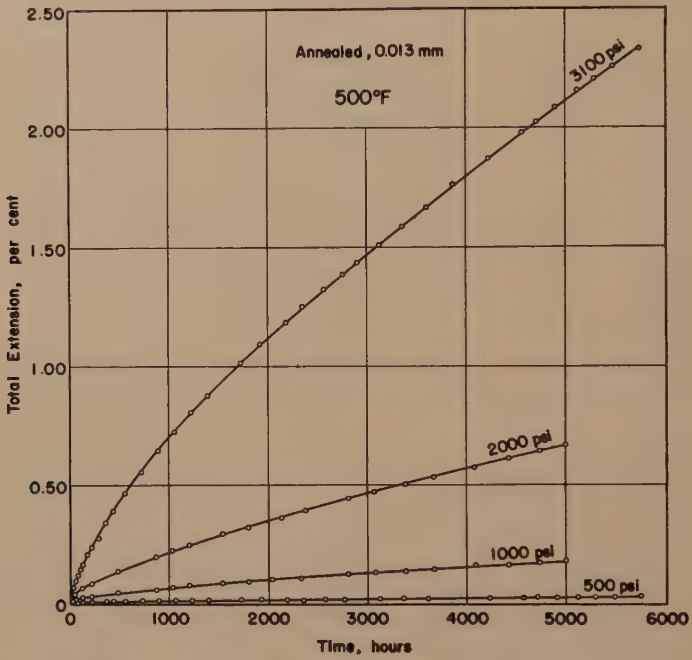

FIG. 10.—TIME-EXTENSION CURVES AT 500°F. FOR ANNEALED TEMPER.

The effect of temperature on the creep strength of both materials is further illustrated in Fig. 15. The relative change in the stresses producing a creep rate of 0.01 per cent per 1000 hr. in the two materials appears graphically as the convergence of the two curves in this figure. This unequal decrease in creep strength with increasing temperature may be attributed to differences in the structural stability of the two materials at the elevated temperatures. Exposures at 300°, 400°, and 500°F. do not affect the structure of the annealed material. The drawn temper, on the other hand, undergoes recrystallization in varying degrees at all three of these temperatures, as previously discussed. The drawn structure is only very slightly affected by exposure at 300°F. because the rate of recrystallization at that temperature is exceedingly low. At 500°F., however, the rate of recrystallization is very high, changing the drawn wire in a few hours to a material of virtually the same structure as that of the originally annealed temper. This transformation was essentially complete at 500°F. even before the creep tests were started because all specimens were held at temperature for 24 hr. before the load was applied, in order to establish temperature equilibrium. The similarity at 500°F. of the structures of the two initially different materials accounts for their almost identical creep behavior. (Compare the curves of Figs. 10 and 13.) At 400°F. the rate of recrystallization lies between the very low and the very high rates at 300° and 500°F., respectively. This has a direct bearing on the creep rate because creep rate varies with structure. Since the rates of deformation in worked and recrystallized grains are not the same, the average creep rate is dependent on the relative amounts of each in the structure. The drawn temper has a greater creep strength at 400°F. than the annealed temper, by virtue of the fact that recrystallization does not proceed to completion during the creep test. Even after 5000 or 6000 hr. of exposure there is still an appreciable proportion of unrecrystallized grains in the structure, which accounts for the higher creep strength.

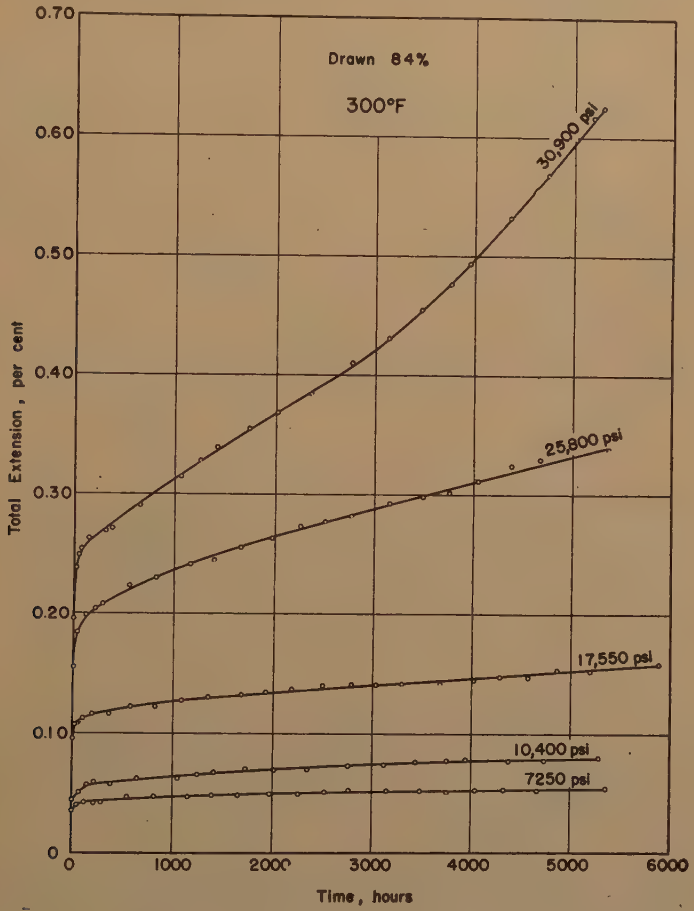

FIG. 11.—TIME-EXTENSION CURVES AT 300°F. FOR DRAWN TEMPER.

The creep rate of 0.01 per cent per 1000 hr. was chosen as a basis of comparison in Fig. 15 because it is frequently used as a criterion of creep strength for purposes of design. This rate produces an extension of 1 per cent in somewhat more than 11 years. It was among the criteria used in establishing the maximum allowable stresses at various temperatures for nonferrous materials in a recently revised version of Table U-3 of the A.S.M.E. Boiler Code.[8] The copper of the present investigation is included among the several types of copper within the scope of Table U-3 and it is therefore interesting to compare the pertinent values in that table with the present creep test results. This has been done in Fig. 16, where the stresses, required to produce a creep rate of 0.01 per cent per 1000 hr., taken from Table 3, are plotted as a function of temperature along with the allowable stresses for annealed, light-drawn and hard-drawn copper given in Table U-3. It is apparent that the allowable stresses for cold-drawn material are very conservative for temperatures up to 400°F. with respect to the present test results.

The allowable stresses for the annealed condition are also conservative with respect to the present test results up to 300°F. At 350°F. and 400°F., however, the listed stresses for this temper are greater than the corresponding values derived in the present work. In this connection, it is to be noted that, in Table U-3, the revised value of allowable stress, 3000 lb. per sq. in., for annealed copper at 400°F. (or 406°F.) has been reduced from 4000 lb. per sq. in., a value previously in effect for a considerable number of years and presumably used successfully.

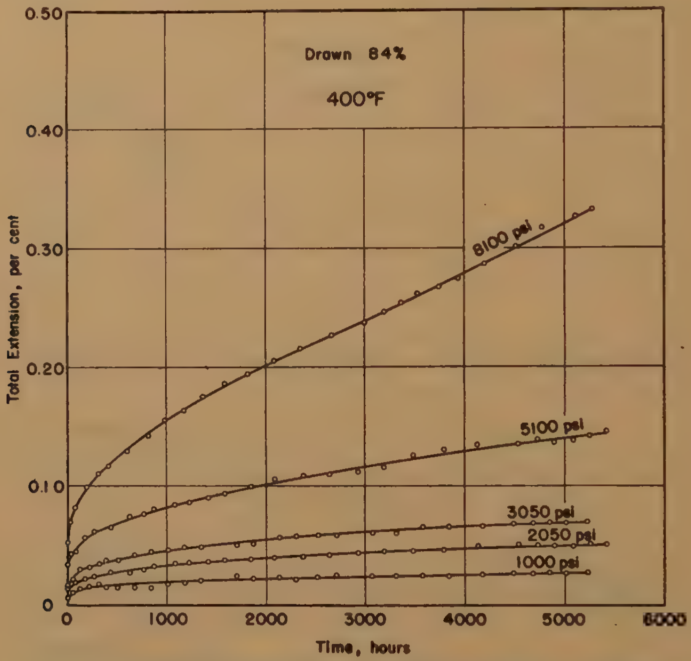

FIG. 12.—TIME-EXTENSION CURVES AT 400°F. FOR DRAWN TEMPER.

Some creep data on copper, including stress-creep rate plots, are recorded in the literature[9] for tests of about 1000 hr. duration. The plots of stress-creep rate at 1000 and 5000 hr. in Figs. 17 and 18 demonstrate the importance of the length of testing time in the evaluation of the creep characteristics of the present materials. These curves are based on actual measure-

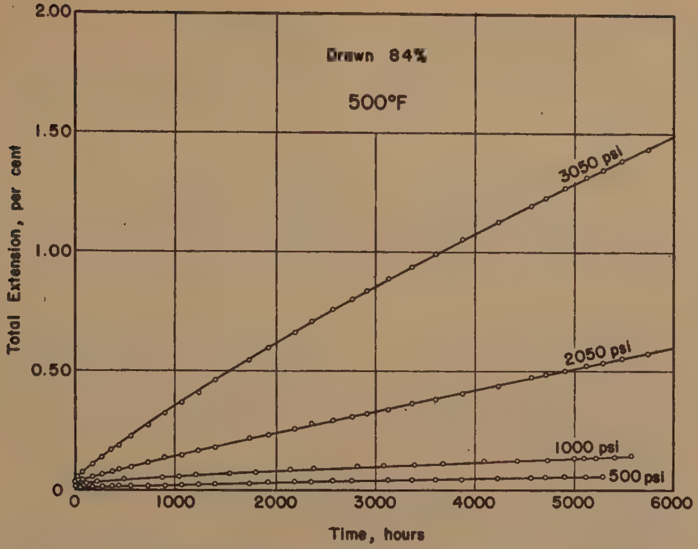

FIG. 13.—TIME-EXTENSION CURVES AT 500°F. FOR DRAWN TEMPER.

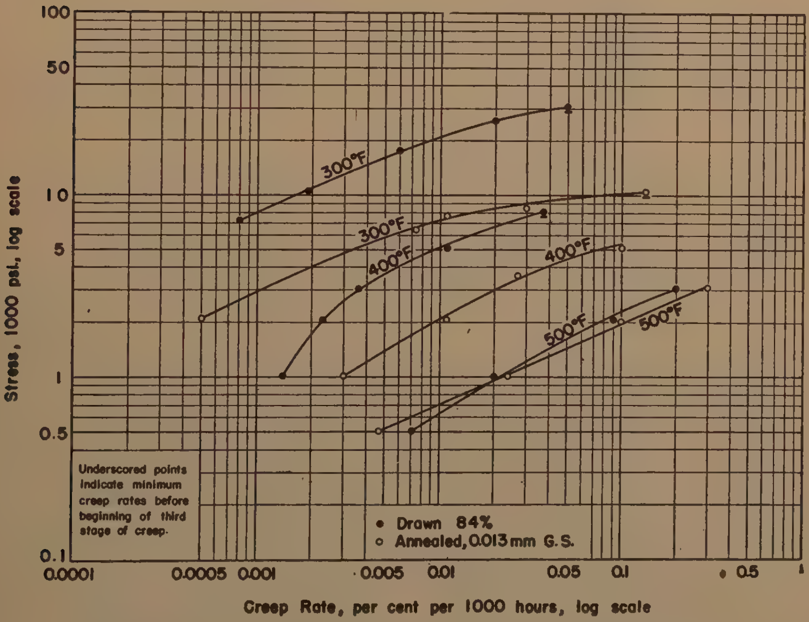

FIG. 14.—CREEP RATE AS FUNCTION OF STRESS.
Creep rates taken at end of test period except as otherwise indicated.

ments of the primary creep curves and do not involve any extrapolation. There is a marked deviation between the curves of each corresponding pair, which in four of the six pairs is greater at the lower stresses. In view of this deviation, it is apparent that the results based on the shorter time are of considerably less value for purposes of design than those based on the longer time. In addition, it will be noted that there is somewhat more scatter of the points representing creep rates at 1000 hr. Anomalies in the results of short-time creep tests have also been observed by others,[5,10] who noted that the early stage of the creep process is not always consistent even for duplicate tests that eventually yield the same steady creep rate. This has been attributed to such phenomena as localized deformation, adjustment of stress distribution and grain rotation.

The variation of creep rate with time for all tests is shown in Fig. 19. A steady creep rate was attained in 12 of the 28 tests represented and these 12 include 2 that subsequently progressed into the third stage of creep. These creep rate-time curves make it possible to estimate approximately how long most of the remaining 16 tests should have been continued in order to determine the true steady creep rates. It is indicated that periods of time approaching almost 20,000 hr. would have been necessary in order to reach a steady creep rate in some of the tests, but in most instances a shorter length of time would have been sufficient. With some exception, only tests of very low creep rate need to be

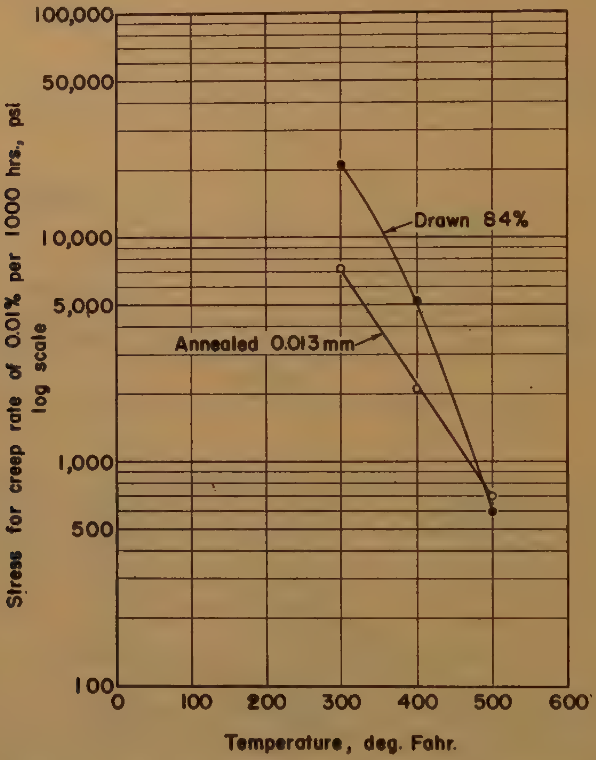

FIG. 15.—CREEP STRENGTH AS FUNCTION OF TEMPERATURE.

continued for more than about 7000 or 8000 hr. to attain the steady rate, but since these usually are of only limited practical value, their termination before a steady creep rate is attained should not lead to serious consequences. On the other hand, however, tests involving stresses that produce moderate creep rates might well be continued until the rate of extension is essentially constant. It is possible to extrapolate to the stage of steady creep rate those curves of Fig. 19 that have not reached such a rate within the testing time, although the operation requires considerable imagination in several instances. It is found that extrapolations usually are necessary in the range of low stresses and creep rates, which is in accord with the common observation that the time required to attain a steady creep rate increases as the applied stress decreases. The new set of creep-rate values thus obtained are plotted in Fig. 20, where it is evident that most of the data are more closely represented by straight lines, as drawn, than by curves. The only great deviation appears to be at the lower stresses and rates where accuracy is the least. On this basis a complicated mathematical analysis of the log-log curves becomes unnecessary.

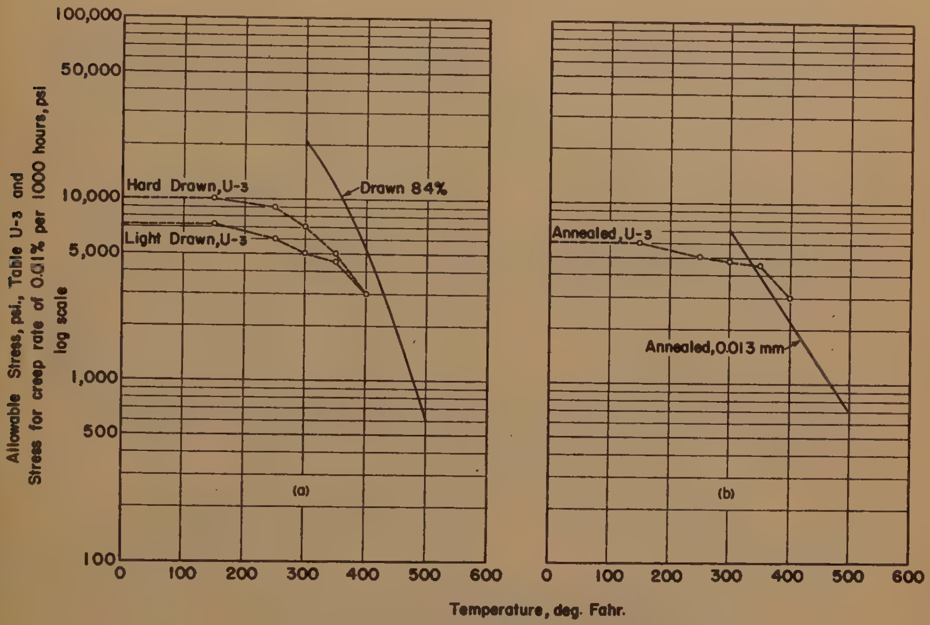

FIG. 16.—CREEP STRENGTH AS FUNCTION OF TEMPERATURE.
Curves of Fig. 15 are compared with data from A.S.M.E. Boiler Code Table U-3.

Of primary importance, however, in the analysis of the logarithmic stress-creep rate relationship, either as a curve or straight line, is the need for a clear understanding of what each point on the plot represents in terms of the extension-time curve from which it is derived. When a very long time is required to attain a constant creep rate, it may be of great value to know the actual course of the creep curve over an extended period. This makes it desirable to obtain extensive primary creep data and there appears to be no way at present of avoiding or lessening appreciably the long experimental procedure involved in securing such data.

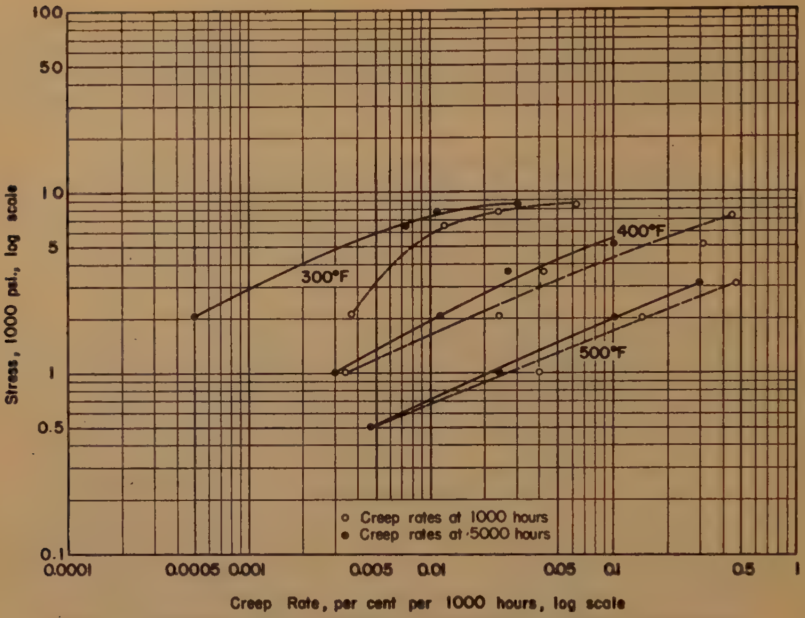

FIG. 17.—CREEP RATE AS FUNCTION OF STRESS FOR ANNEALED TEMPER. Creep rates taken at 1000 and 5000 hours as indicated.

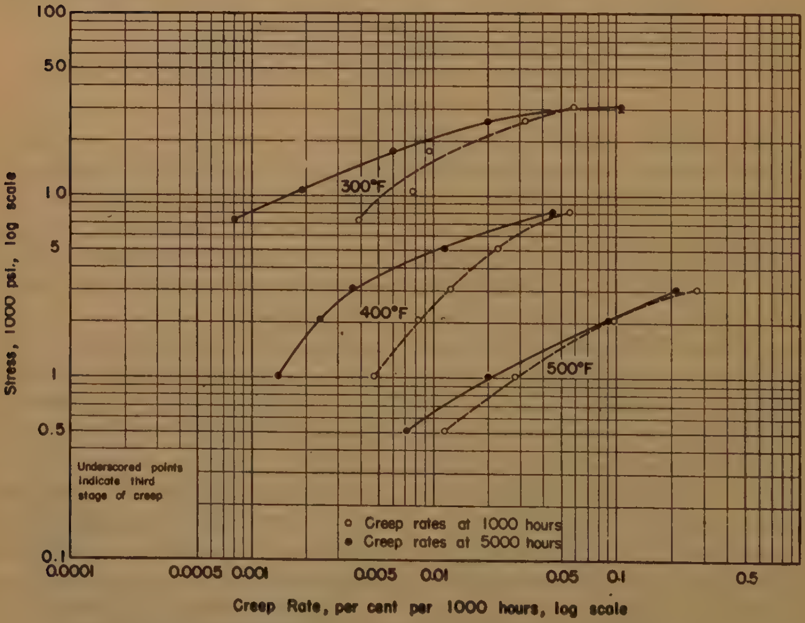

FIG. 18.—CREEP RATE AS FUNCTION OF STRESS FOR DRAWN TEMPER. Creep rates taken at 1000 and 5000 hours as indicated.

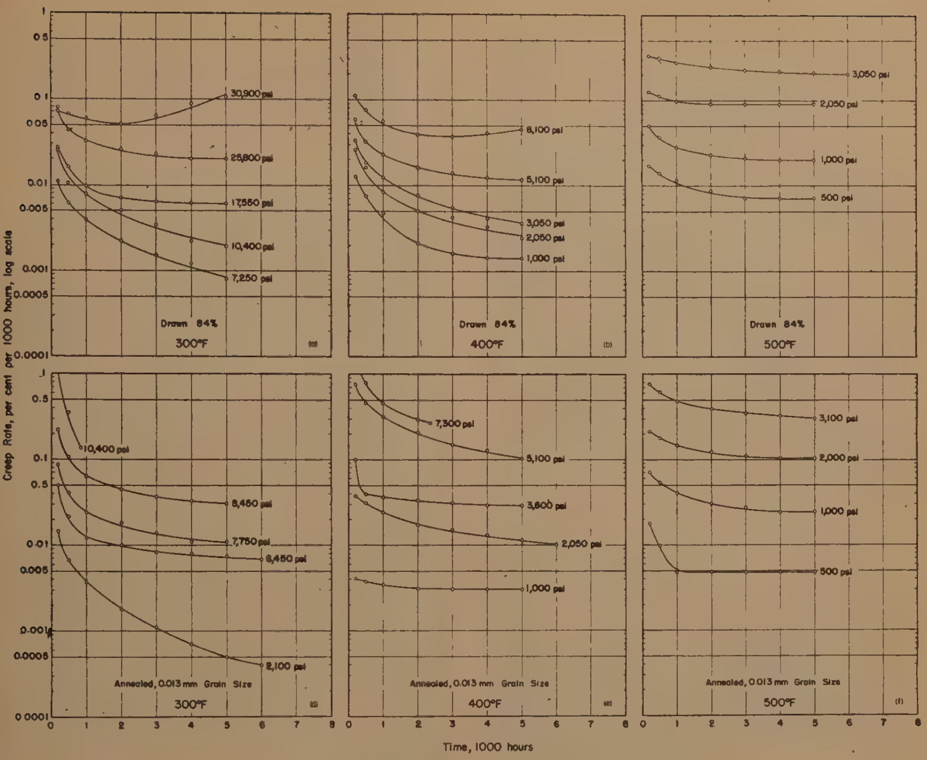

FIG. 19.—CREEP RATE AS FUNCTION OF TIME.

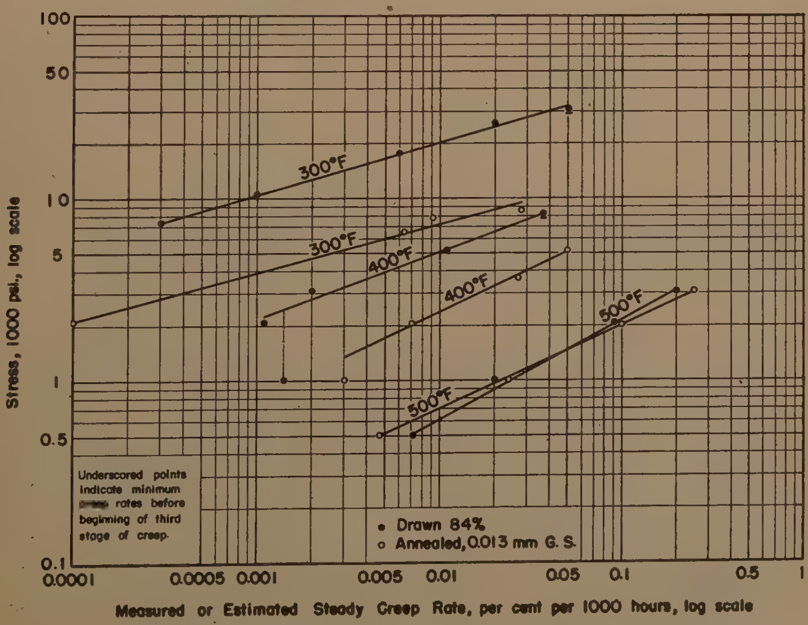

FIG. 20.—CREEP RATE AS FUNCTION OF STRESS FOR DRAWN TEMPER. Creep rates taken from test data or from extrapolation of curves in Fig. 19.

SUMMARY

Creep characteristics at 300°, 400° and 500°F. of phosphorized (0.008 per cent P) copper wire as annealed to a grain size of 0.013 mm. and as drawn 84 per cent and straightened are reported. The creep resistance of the drawn wire is far superior to that of the annealed material at 300°F., but progressive recrystallization of the former operates to reduce this difference as temperature increases until, at 500°F., the creep characteristics of the two initially different materials become essentially the same. The importance of extensive primary creep data derived from tests of long duration is confirmed.

ACKNOWLEDGMENTS

The authors wish to acknowledge the interest of Dr. D. K. Crampton in the work, the assistance of Mr. J. S. Porter and Mrs. Nora Hirsch in obtaining some of the test data and of Mr. H. Hughson in the preparation of the photomicrographs. Thanks are extended to the Chase Brass and Copper Co. for permission to publish the results.

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DISCUSSION

(E. E. Schumacher presiding)

J. J. KANTER.*—The authors of this paper have demonstrated that at 500°F. their alloy will elongate, under appropriately adjusted stress, one or two per cent over a period of 6000 hr. Then they show that after the alloy has so elongated, it will still elongate another 40 per cent if it is tested at ordinary temperature. I should like to ask the authors how much more than 2 per cent over a period of 6000 hr. their alloy will elongate at 500°F.

H. L. BURGHOFF.—We do not know, because we have not carried out stress-rupture tests on this material. I believe your point concerning the desirability of stress-rupture testing is very well taken. In the material that we have subsequently tested we have not seen any signs of deterioration. We do not know how much further it is possible to go beyond the 2 per cent before finding grain-boundary separation. We have not encountered any under the conditions of the test.

W. E. KINGSTON.†—Is this particular type of copper susceptible to strain-aging, and if so at those comparatively low temperatures, is that going to affect the shape of the curve? By strain-aging I mean the phenomena that certain ferrous alloys show in which the resistance to deformation increases suddenly during the low-temperature creep cycle, apparently due to some precipitation type of reaction, perhaps analogous to hydrogen embrittlement.

H. L. BURGHOFF.—I believe that this material is not subject to strain-aging of this type. It is very high in copper content, of course, nearly 100 per cent. There are some very minor impurities and it carries a small amount of phosphorus, which, unless it is present as an oxide, should be in solid solution well within the solubility limits. I believe it does not precipitate.

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* Crane Co., Chicago, Illinois.

† Sylvania Electric Products Inc., Bayside, N. Y.

A. J. SMITH.*—I wonder a little about the early portions of some of the curves in Fig. 19. In the bottom figure to the right, in the lowest curve, there is a very marked drop before the flattening out. The same applies at 500°F. in the figure just adjoining to the left. At 400°, 3600 lb. per sq. in., the initial portion of the curve, there is also a marked drop—a marked flattening out. I wonder if you have information as to just how that is produced.

H. L. BURGHOFF.—The actual values for these curves are obtained by determining the slope of the primary creep curve at suitable intervals. In regard to the lowest curve of the lower right-hand graph of Fig. 19, it should be appreciated that the creep rate is very low and therefore difficult to determine accurately. The instances where most of the curve is horizontal—that is, where creep rate is constant—represent the exceptions that were encountered in our tests. Of course, it is well recognized that a little time is required for material to determine just how it is going to creep. A number of discourses on creep have pointed out that the early portions of creep curves may not always be consistent within a group.

H. F. MCCULLOUGH.†—Are there any data on creep of oxygen-free high-conductivity copper or ordinary tough-pitch copper, as compared with this copper containing 0.008 per cent phosphorus?

H. L. BURGHOFF.—We have such work in process, but it is a little early to tell what the results are going to be. Both tough-pitch and oxygen-free copper have lower creep resistance than phosphorized copper. We will have the data within the next year or so.

H. L. EISELSTEIN.‡—I should like to ask about another type of instability. In the literature recently order-disorder phenomena have been written up, and I should like to know whether anyone has run creep tests on any alloys that exhibit the phenomena, sometimes called second-order phase changes. I am primarily interested in what happens during the creep test in an alloy that exhibits order-disorder phenomena. Does the material become embrittled? Does it become more creep resistant, or what happens?

H. L. BURGHOFF.—I can answer only for ourselves. We have not made any tests on such alloys, at least knowingly. There has been some thought that some of the brasses do have an ordered structure, particularly brasses containing the beta phase, but we have nothing to contribute to that.

R. B. GORDON.*—We have not run creep tests on anything undergoing order-disorder but I think it is quite generally true that any structural change accelerates creep. I think we have seen an example of that in the data presented here in Fig. 14. At 400°F. the cold-rolled material has a steeper slope on the curve of stress versus creep rate, and I think this may be due to the recrystallization that occurred.

I have one other question. I wonder if the difference at 500°F. might not be due to a difference in the grain size of the annealed material and the recrystallized drawn material. There is a small but appreciable difference in the slope of those two curves drawn through points at four different stresses.

H. L. BURGHOFF.—Grain size is an important factor in determining the creep characteristics of copper-base alloys, and the present material may be considered an alloy even though it is so nearly pure copper.

These two curves for 500°F. do cross over each other and thus have a definite difference in slope. The grain sizes are not greatly different, and I am inclined to believe one curve drawn through all the points at 500°F. would be a fair representation of creep characteristics of this phosphorized copper for grain size in that range.

If we had had a definitely different order of grain size for one or the other, we might have shown a greater separation of the two curves.

MEMBER.—Is there a study on the effect of hysteresis in metals such as are used in making brass or bronze bellows?

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* Lunkenheimer Company, Cincinnati, Ohio.

† General Electric Co., Schenectady, N. Y.

‡ International Nickel Co., Huntington, W. Va.

* Research Laboratory, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pennsylvania.

H. L. Burghoff.—Hysteresis is an effect that can be encountered in many copper alloys as well as in other types. The extent of hysteresis, I presume, would be governed by the operating conditions, including just how long the bellows might be retained at a stress. I do not know where to point to any quantitative data on the subject. It is a problem that is to be recognized, however.

W. E. Kingston.—Would the authors care to describe the equipment used in more detail; that is, the methods utilized to ensure uniform temperature distribution over the specimen?

A. I. Blank.—The furnaces have been described in greater detail in another paper listed in the references. Briefly, the furnaces are sheet-iron containers, lined with insulating brick. The interior is divided into two channels by a horizontal baffle plate. Resistance units at either end heat the air, which is circulated through the channels by blowers. Numerous small baffle plates set at about 45° deflect the stream of hot air from the heaters to prevent it from rising too rapidly. The interior is about 5 ft. long, 5 in. wide and 20 in. high. The creep specimen extends vertically through the furnace with about 10 in. of it in a region of very closely controlled temperature. The furnace temperatures are controlled automatically by potentiometric controllers at 400° and 500°F. and by a mercury thermal regulator at 300°F. Time variation of temperature does not exceed 2°F. and the distribution of temperature throughout the length of the furnace does not exceed 5°F. This is perhaps not as important as the variation of temperature of the individual specimens, and it does not exceed 5°F. over the 10-in. gauge length. The temperature distribution thus obtained is well within the limits of the A.S.T.M. Standard Recommended Practice for conducting creep tests.

F. P. Huston, Jr.*—In Fig. 20, in which the extrapolated stress versus secondary creep-rate curves are shown, how do you reconcile the linear curve for 400° for the drawn material with that shown in the original curve, Fig. 14, in which the initial portion follows the viscous condition and falls into a decreasing rate? Which of these two figures would you use in design work?

H. L. Burghoff.—The curves shown in Fig. 14 are based upon the actual creep rates in effect at the end of the test period, which lies between 5000 and 6000 hr. There has been no extrapolation involved in arriving at the plotted values. They represent the actual test data, and I dare say that is what should be adhered to for the safest design. One can use Fig. 20—always remembering, of course, what the primary creep curves look like.

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* International Nickel Co., Huntington, West Virginia.

Creep Properties of Cold-drawn Annealed Monel and Inconel

By B. B. Betty,* H. L. Eiselstein,† and F. P. Huston, Jr.,† Junior Member A.I.M.E.

(Cleveland Meeting, October 1944)

An extensive program for the establishment of creep data on high-nickel alloys has been in progress during the past seven years. This paper presents the accumulated data on two solid solution alloys, cold-drawn, annealed Monel and cold-drawn, annealed Inconel. Data on these two alloys in other conditions will be published at a later date.

Monel, a nickel-copper alloy, is normally considered a corrosion-resistant material, but it will be shown that it also has considerable creep strength, validating its use at temperatures up to and including 900°F. Inconel, a nickel-chromium-iron alloy, is definitely a heat-resisting alloy possessing good creep strength and oxidation resistance up to 1100°F., and because of its oxidization resistance has been used successfully at much higher temperatures for lightly stressed parts.

The literature contains but meager data on the creep properties of high-nickel alloys. However, Bennett and McAdam have presented a substantial quantity of creep data for cold-drawn Monel.[1] The material as tested was not representative of mill production for it was cold-drawn to a reduction of area of 40 per cent as against 13 per cent, which is the mill standard for Monel.

Twenty-two individual tests were run on each alloy in the investigation described in the following pages. The data and curves presented herein represent an integration of all the tests to obtain the most accurate picture of the creep properties of these alloys.

Neither of the two alloys was found to be embrittled by the combination of temperature and stress, as evaluated by room-temperature tensile and impact tests that were made following creep testing. These data indicate that no tendency toward embrittlement exists.

It is recommended that 6300 lb. per sq. in. be used as a working stress for cold-drawn, annealed Monel at 900°F. and 13,200 lb. per sq. in. for cold-drawn, annealed Inconel at the same temperature. Table 8 lists recommended working stresses, based on 80 per cent of the stress to produce a minimum creep rate of 0.01 per cent per 1000 hr., for Monel and some steels.

Equipment

The equipment used for these tests consists of Colville creep-testing machines manufactured by the Tinius Olsen Testing Machine Co. The load is adjusted, depending on the stress level, to give an error in the stress of not more than ±0.1 per cent. This is based on considerations of lever sensitivity and the stress used for the standard (A.S.T.M. Tentative Standard E22-38T) 0.505-in. diameter creep specimen having a 2-in. gauge length. The single-specimen furnaces are provided with primary and secondary windings, from

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[1] References are at the end of the paper.

which sufficient taps are led so that adjustments in temperature distribution can be made by adding shunts or external resistances to various sections of the windings.

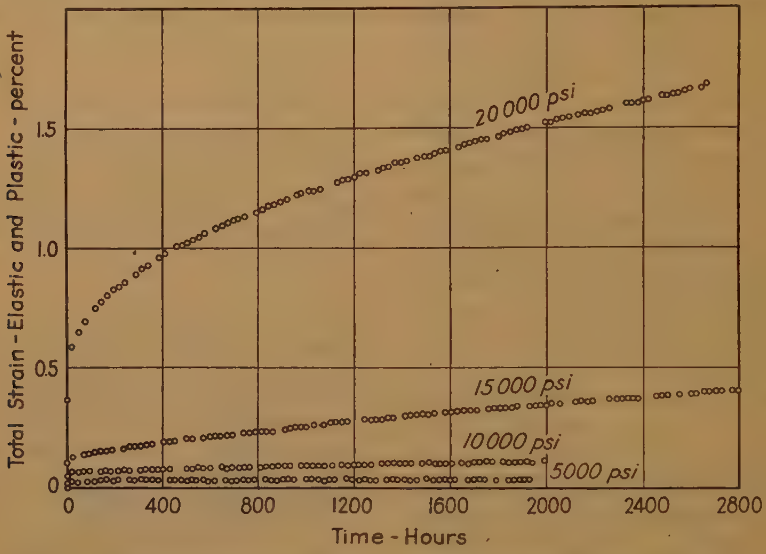

Fig. 1.—Creep-time curves for cold-drawn, annealed Monel at 900°F.

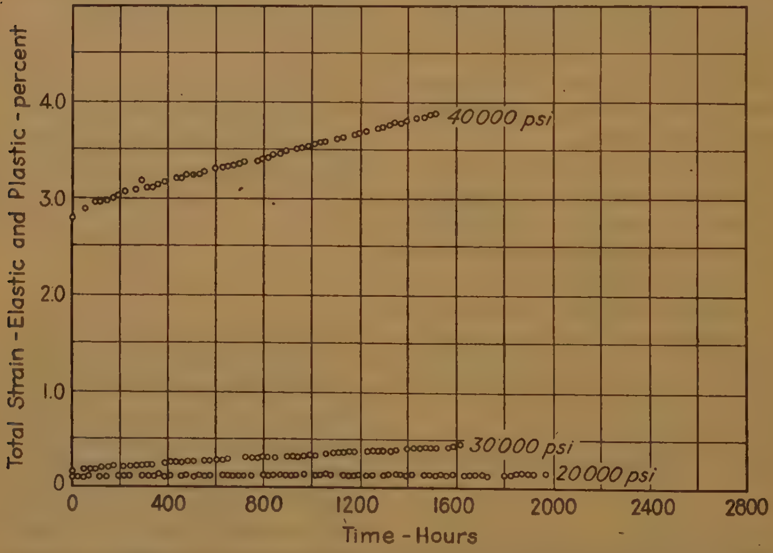

Fig. 2.—Creep-time curves for cold-drawn, annealed Inconel at 900°F.

Each furnace is connected to an individual power and control source and the power and control sources for the 10 furnaces are grouped on a central panel.

An Alumel-Chromel thermocouple mounted close to the hottest section of each winding is connected to the controlling pyrometer for that frame. The pyrometer actuates a two-position relay controlling the power input to the furnace. The furnace power is supplied by an 865-va. stepdown transformer operating from a 220-volt line and providing voltage taps from 30 to 75 volts in 3-volt increments. The furnace temperature is maintained by adjusting the taps cut in on two stages of the transformer. The furnace temperature is controlled by a relay, actuated by a pyrometer, cutting in alternately on the high and low transformer taps so that the furnace control couple fluctuates between ±3°F. of the pyrometer setting. An ammeter is provided in the circuit to aid in the selection of the voltage taps.

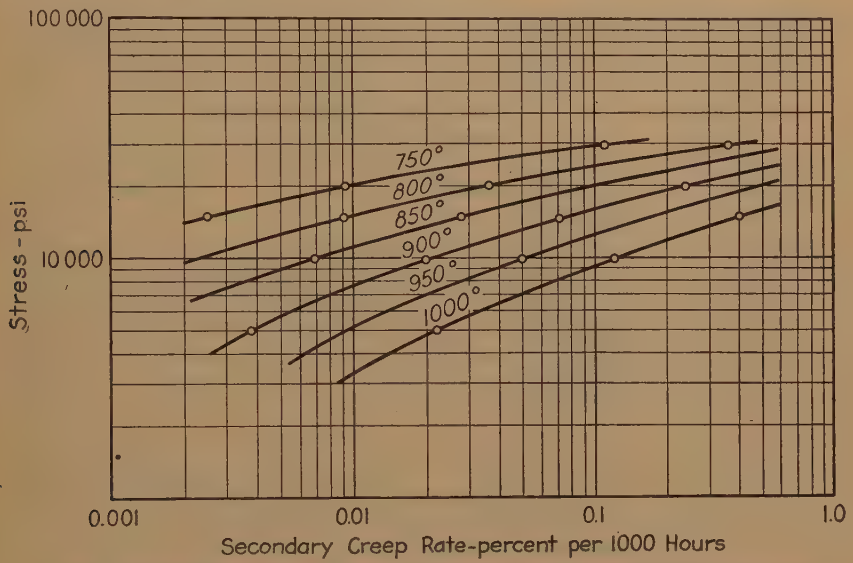

FIG. 3.—STRESS-CREEP RATE RELATIONS FOR COLD-DRAWN, ANNEALED MONEL.

The controlling equipment consists of four Tag Celectray and six Leeds and Northrup indicating pyrometers. In addition, three Leeds and Northrup 4-point recording pyrometers are provided.

The creep extensions are indicated by means of sliding platinum extensometer strips fastened on opposite shoulders of the creep specimen and read by a cathetometer fitted with a filar eyepiece, the sensitivity of which is ±0.00059 inches.

Degree of Temperature Control

As stated previously, the furnace-winding control couple, and consequently the indicating pyrometer, is maintained to within ±3°F. of the selected temperature for the winding. However, this is a delicate adjustment, in which it is necessary that the duration of high and low power intervals be made approximately equal. Under these conditions the temperature cycle for the specimen is damped sufficiently by conduction of heat from the winding through the muffle to the specimen that the specimen temperature is held constant to within ±1°F. The temperature gradient over the 2-in. gauge length is adjusted to within 2°F. for the duration of the test.

Five thermocouples are mounted on each specimen, as follows; one each at the top and bottom of the gauge length, one in the center, and one each in holes drilled 1¾ in. deep into the top and bottom shoulders of the specimen. The thermocouple inserted in the top hole is connected to a recording pyrometer, thus providing a continuous record of the specimen temperature cycle throughout the test. The three thermocouples on the gauge length are read twice daily during test. A Leeds and Northrup portable potentiometer, standardized before each reading, is used to obtain the temperature indicated by the thermocouples. Adjustments are made as required at these times.

TECHNIQUE AND HANDLING OF DATA

The back and front extensions were read daily and the average percentage of elongation plotted versus time of test. When the minimum creep rate (secondary) was well established, the elastic extension was obtained by removing the load and obtaining a reading immediately to avoid any plastic recovery. All data were handled so as to obtain the utmost accuracy, depending on the conditions of test, precision of measurements and considerations of temperature differentials from day to day. These considerations were instituted not only in handling the daily readings but in the choice of a suitable scale to use in plotting.

The data were plotted as creep versus time, log creep rate versus time, log creep rate versus the reciprocal of the absolute temperature (Kanter diagram), log stress versus temperature, and log stress versus log minimum creep rate in arriving at the most suitable representation. In some cases one diagram presented an easier method of adjustment than others, therefore all available methods were considered and tried in analyzing the data. Primary consideration was given to the establishment of what were considered to be representative families of curves rather than to placing undue importance on any one value.

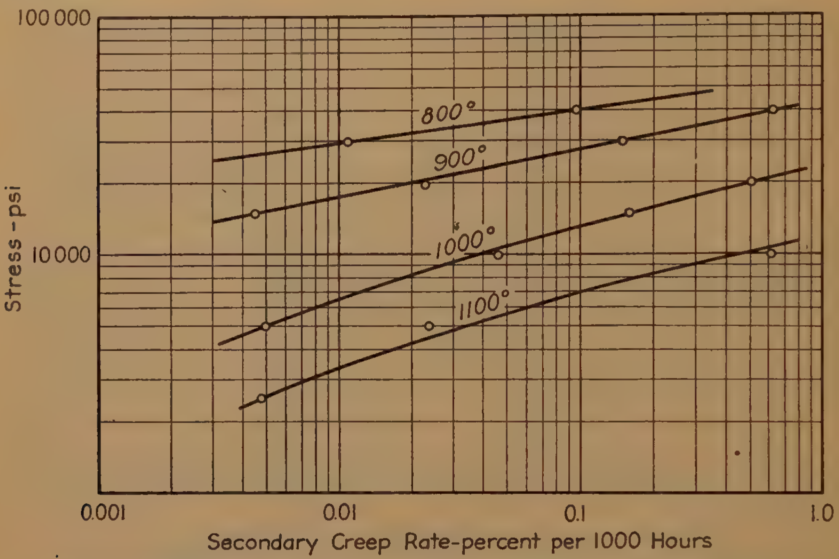

FIG. 4.—STRESS-CREEP RATE RELATIONS FOR COLD-DRAWN, ANNEALED INCONEL.

REPRESENTATIVE MATERIAL

The materials used for these tests were selected from representative commercial melts known to possess normal chemical composition and mechanical properties. The materials selected were hot-rolled from billets to 1-in. diameter rods, annealed and pickled. The hot-rolled rods in turn were cold-drawn to $^{13}\!/_{16}$-in. diameter rods, annealed and pickled, and finally drawn to $^{3}\!/_{4}$-in. diameter rods, entailing a cold reduction of 13 per cent in the last operation. The chemical compositions of these two materials are given in Table 1.

The specimens were annealed in the laboratory to a condition representative of the respective alloys in the commercial "cold-drawn, annealed" condition. The annealing treatment given the two cold-drawn alloys was 3 hr. at 1500°F. followed by air cooling for the Monel, and 3 hr. at 1750°F. followed by air cooling for the Inconel.

TABLE 1.—*Chemical Composition*
PER CENT

Alloy	C	Mn	Fe	S	Si	Cu	Ni	Cr
Monel	0.17	1.05	1.20	0.005	0.05	29.76	67.73	
Inconel	0.05	0.29	6.29	0.014	0.16	0.31	79.50	13.41

CREEP STRENGTH

The results of 44 creep tests are reported. As it would not be practical to include the individual curves, representative families at one temperature level (900°F.) are shown for the cold-drawn, annealed alloys in Figs. 1 and 2. The data necessary for a modified McVetty analysis,[2] in which the equation,

$$\text{Creep} = e_0 + vt$$

where e_0 = a constant (intercept for zero time on creep-time plot),
v = minimum creep rate,
t = time

is used to obtain families of curves for stress versus total strain (elastic plus plastic) for various time intervals at constant temperature, are given in Tables 2 and 3; also, the initial extension, total extension (elastic plus plastic), and total duration of test.

The family of curves for log stress versus log minimum creep rate for the cold-drawn, annealed alloys are shown in Figs. 3 and 4. Both families are well defined.

The factors involved in the McVetty analysis were plotted as stress versus log intercept e_0 (elastic plus plastic strain) in Figs. 5 and 6. These curves substantiate McVetty[3] in that they indicate that the intercept e_0 is a hyperbolic sine function of stress at relatively low stresses but rises to a maximum value at a high stress, beyond which it probably decreases.

Fig. 7 presents the essential data. The relative creep strengths of the two alloys are shown in a clear, well-defined form by a plot of log stress versus temperature, on which data for both alloys are indicated for a minimum creep rate of 0.01 per cent per 1000 hr. It should be noted that in the temperature range considered cold-drawn, annealed Inconel can be used at stresses approximately twice those that would be safe for cold-drawn, annealed Monel.

MECHANICAL PROPERTIES

After the creep tests were completed, the specimens were either tested as short-time, static tensile tests or machined into impact specimens and broken. The tensile properties of the original materials and the specimens after creep testing are listed in Table 4. These data do not show any decrease in the strength values, and, more important, show no loss of ductility. The yield-strength values show that some of the specimens had strain-hardened considerably during the creep test.

In carrying out the impact testing of the creep materials, two considerations had to be taken into account. In the first place, it was not possible to machine the 0.394-in. square standard Izod or Charpy impact specimen from the 0.505-in. creep specimen. In the second place, it was known that the standard impact specimens were not always suitable for testing these alloys, because of their great toughness and ductility. Many of the standard impact specimens could not be broken by a single impact blow.

Accordingly, some experimental testing was done for the purpose of designing an impact specimen that would spread the resulting impact values over the available 120 ft-lb. of the Izod impact machine with the most ductile conditions of the nickel alloys at the top of the range and

TABLE 2.—*Creep Data for Cold-drawn, Annealed Monel*[a]

Specimen	Temperature, Deg. F.	Stress, Lb. per Sq. In.	e_0, Per Cent	v,[b] Per Cent, 10^3 Hr.	Initial Extension, Per Cent	Total Extension, Per Cent	Duration of Test, Hr.
B10CDA	750	15,000	0.114	0.0025	0.092	0.119	1,896
B5CDA	750	20,000	0.320	0.0093		0.343	1,862
B6CDA	750	30,000	0.720	0.11		0.870	1,960
B13CDA	800	15,000	0.091	0.0061	0.071	0.101	1,751
B11CDA	800	15,000	0.106	0.0092	0.082	0.123	1,850
B10CDA	800	20,000	0.321	0.081	0.215	0.484	2,007
B19CDA	800	20,000	0.340	0.036	0.186	0.456	2,884
B16CDA	800	30,000	3.650	0.333	2.710	4.300	2,498
B8CDA	850	10,000	0.078	0.0069	0.054	0.092	1,914
B9CDA	850	15,000	0.155	0.028	0.105	9.206	1,810
B2CDA	850	20,000	0.683	0.179	0.325	1.061	2,113
B1CDA	900	5,000	0.028	0.0038	0.013	0.035	1,919
B15CDA	900	10,000	0.069	0.0205	0.042	0.110	1,989
B7CDA	900	10,000	0.079	0.048	0.075	0.156	2,022
B12CDA	900	15,000	0.150	0.102	0.076	0.347	1,961
B17CDA	900	15,000	0.205	0.071	0.100	0.406	2,790
B18CDA	900	20,000	1.038	0.240	0.364	1.678	2,678
B20CDA	950	10,000	0.098	0.049	0.055	0.216	2,441
B4CDA	1000	5,000	0.070	0.021	0.034	0.206	2,375
B21CDA	1000	10,000	0.160	0.121	0.074	0.436	2,281
B23CDA	1000	15,000	0.570	0.400	0.145	1.785	2,908

[a] All data except v are good to within ±0.001 per cent.
[b] v = minimum creep rate, per cent per 1000 hours.

TABLE 3.—*Creep Data for Cold-drawn, Annealed Inconel*[a]

Specimen	Temperature Deg. F.	Stress, Lb. per Sq. In.	e_0, Per Cent	v,[b] Per Cent, 10^3 Hr.	Initial Extension, Per Cent	Total Extension, Per Cent	Duration of Test, Hr.
NX19CDA	800	30,000	0.888	0.011	0.862	0.906	1870
NX11CDA	800	40,000	2.859	0.097	2.808	3.040	1861
NX17CDA	800	50,000	1.422	0.023	1.370	1.470	1945
NX5CDA	900	15,000	0.092	0.045	0.074	0.100	1876
NX9CDA	900	20,000	0.110	0.023	0.090	0.150	1969
NX3CDA	900	30,000	0.186	0.15	0.153	0.447	1610
NX2CDA	900	30,000	0.702	0.12	0.659	0.923	1906
NX8CDA	900	40,000	2.919	0.63	2.780	3.875	1515
NX16CDA	1000	5,000	0.028	0.005	0.024	0.037	1792
NX6CDA	1000	5,000	0.044	0.0072	0.031	0.056	2039
NX15CDA	1000	10,000	0.051	0.056	0.043	0.169	2110
NX7CDA	1000	10,000	0.064	0.045	0.047	0.150	1942
NX4CDA	1000	15,000	0.114	0.16	0.074	0.604	2161
NX18CDA	1000	20,000	0.100	0.51	0.099	0.640	581
NX13CDA	1100	2,500	0.025	0.0048	0.022	0.033	2207
NX12CDA	1100	5,000	0.033	0.024	0.018	0.071	1602
NX10CDA	1100	5,000	0.039	0.020	0.024	0.078	1989
NX7CDA	1100	10,000	0.126	0.63	0.056	0.773	1029

[a] All data except v are good to within ±0.001.
[b] v = minimum creep rate, per cent per 1000 hours.

the less ductile at the lower end. It was found that a 60° V-notch with an 0.01-in. radius at the base, and of such depth that the base of the notch is 0.350-in. diameter, met the requirements fairly well. An approximately straight-line relationship was found to exist between the modified Izod impact test values and the standard Charpy and Izod impact values.

Fig. 8 shows the design of the modified Izod specimen and the position of its notches relative to the creep specimen. Table 5 contains the results of the impact tests made from creep specimens tested at the indicated temperature and stress. Both the Inconel and Monel show good impact resistance after all previous conditions of stress and temperature.

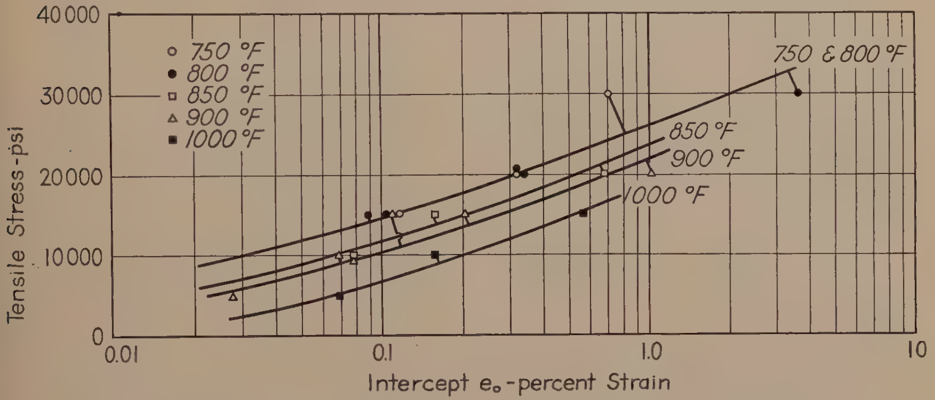

FIG. 5.—STRESS VS. LOG INTERCEPT e_0 FOR COLD-DRAWN, ANNEALED MONEL.

TABLE 4.—*Room-temperature Mechanical Properties of Creep-test Specimens*

Temperature of Creep Test, Deg. F.	Stress Applied during Creep Test, Lb. per Sq. In.	Duration of Test, Hr.	Yield Strength (0.2 Per Cent Set), Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent	Reduction of Area, Per Cent	Hardness, Rockwell B
COLD-DRAWN, ANNEALED MONEL							
80	0	0	26,900	75,800	46	70	66
750	20,000	1862	30,700	78,300	47	68	68
800	30,000	2498	43,600	81,900	45	65	71
850	20,000	2113	31,300	75,500	47	69	66
850	10,000	1914	28,800	76,800	47	69	64
900	15,000	1916	30,000	75,300	47	67	63
900	10,000	1989	27,600	77,500	49	67	66
950	10,000	2441	27,900	76,300	49	65	67
1000	10,000	2281	28,200	73,800	48	66	63
COLD-DRAWN, ANNEALED INCONEL							
80	0	0	35,600	97,300	41	66	79
800	50,000	1945	60,300	101,000	40	65	90
800	30,000	1874	40,800	96,800	43	64	80
900	40,000	1508	57,800	98,000	46	66	90
900	30,000	1900	39,400	96,500	44	67	80
900	20,000	1969	39,400	96,300	45	65	80
1000	20,000	264	40,800	96,600	44	64	80
1000	15,000	2159	36,600	95,500	43	65	80
1000	10,000	1942	36,700	93,700	44	65	80
1100	10,000	576	40,400	98,200	43	65	80
1100	5,000	1602	35,100	94,500	43	65	80
1100	2,500	2205	35,800	96,600	42	65	80

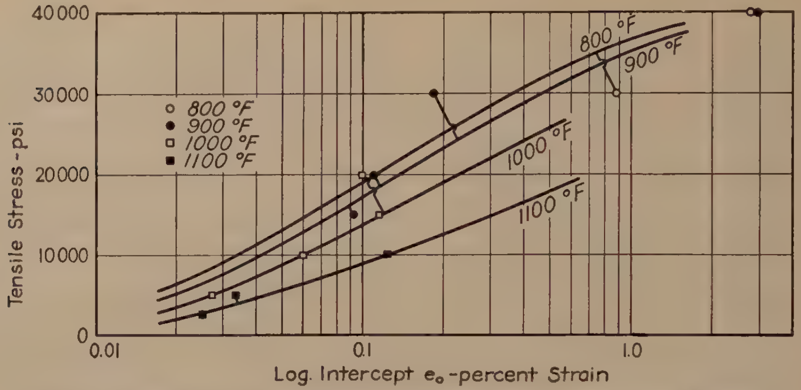

FIG. 6.—STRESS VS. LOG INTERCEPT e_0 FOR COLD-DRAWN, ANNEALED INCONEL.

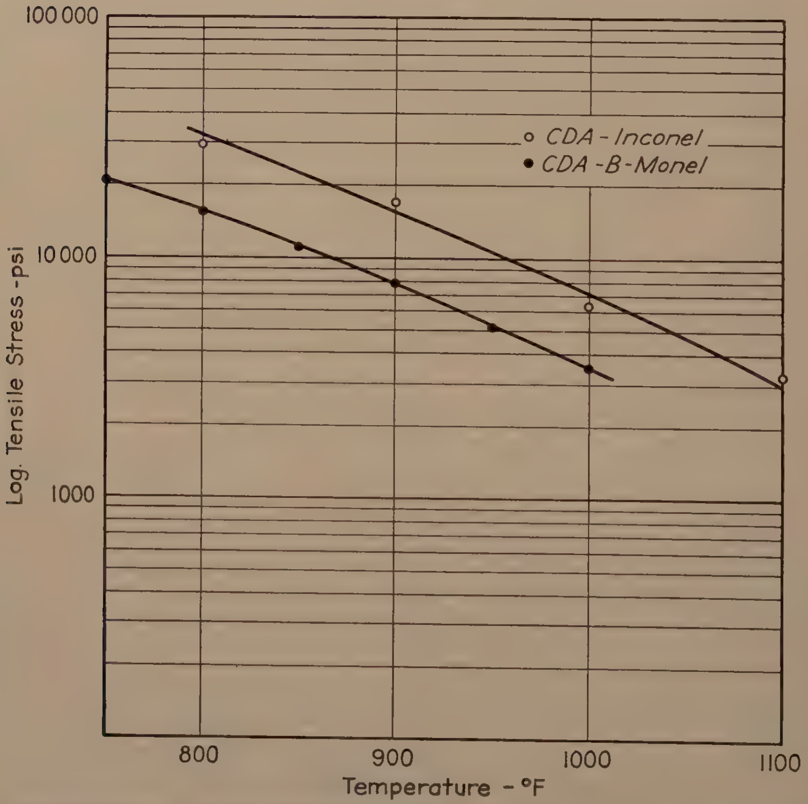

FIG. 7.—LOG STRESS VS. TEMPERATURE FOR CREEP RATE OF 0.01 PER CENT PER 1000 HOURS.

METALLOGRAPHY

Representative photomicrographs of longitudinal sections from the creep specimens are shown in Figs. 9 and 10. The grain structure shown is typical of annealed Monel. Inconel is normally fine grained in most conditions. In this instance the grain size corresponds to a mixture of A.S.T.M. grain-size numbers 6 and 8. In Inconel, as in other alloys containing chromium, chromium carbide is precipitated. The bulk of the chromium carbide in these specimens was precipitated during the 1750°F. anneal. An additional smaller and more finely divided amount of chromium carbide was precipitated during the creep test, outlining the preannealed grain structure of the material.

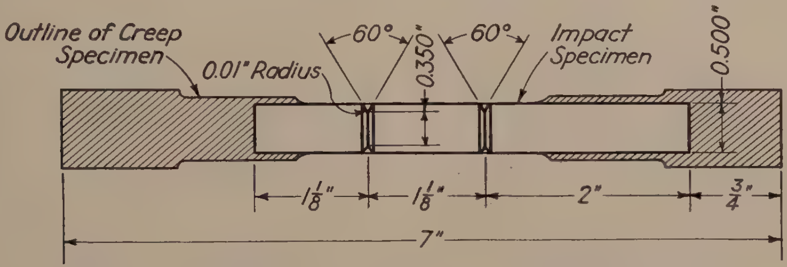

FIG. 8.—POSITION OF ROUND IZOD SPECIMEN IN CREEP-TEST PIECE.

TABLE 5.—*Room-temperature Impact Data for Creep-test Specimens*

Creep Test Temperature, Deg. F.	Creep Test Stress, Lb. per Sq. In.	Creep Test Duration, Hr.	Standard Izod Impact, Ft-lb.	Modified Izod Impact, Ft-lb.	Hardness, Rockwell B
COLD-DRAWN, ANNEALED MONEL					
80	0	0	90–120+	85–87	66
750	30,000	1,960		93–93	70
750	15,000	1,896		84–86	70
800	20,000	2,007		91–94	70
850	15,000	1,810		88–92	67
900	5,000	1,919		85–94	69
COLD-DRAWN, ANNEALED INCONEL					
80	0	0	120+	94–95	79
800	40,000	1,861		76–78	80
900	30,000	1,617		90–96	80
900	15,000	1,876		97–98	80
1000	20,000	582		85–85	80
1000	5,000	2,022		87–89	80
1100	5,000	1,850		101–109	80

THEORETICAL DATA

Enough data were available to make possible an analysis based on W. Kauzmann's equation[4] for rate of creep as a function of stress and temperature. Kauzmann's derivation was based on a rigorous consideration of the mechanism involved in creep, in which Eyring's general theory of shear rates, involving the concept of "units of flow," was utilized. This theory is well presented by Dushman, Dunbar and Huthsteiner[5] along with considerable creep data on several metals and alloys. The creep equation given by them is in a convenient form for computation and is;

$$\log\left(\frac{v}{T}\right) = 10.319 + \frac{\Delta\eta}{4.577} - \frac{Q}{4.577T} + \gamma S$$

Where v = creep rate, strain per second,
T = temperature, deg. Kelvin,
$\Delta\eta$ = change in entropy, cal. per deg. per gram atom,
Q = activation energy per gram atom,
S = tensile stress, dynes per sq. cm.,

TABLE 6.—*n for Cold-drawn, Annealed Monel*

TEST TEMPERATURE, DEG. F.	*n*
750	62
800	65
850	67
900	70
950	72
1000	75

R = gas constant per mol, 1.987 cal. per deg. per gram mol

$4.577 = 2.303R$

Further relations are:

$$\gamma = \frac{J\alpha}{9.154T}$$

$$\alpha = 3.83 \times 10^8 \gamma T$$

$$n = \frac{3.83 \times 10^8 \gamma T}{V_0}$$

where J = conversion factor from ergs to cal.

= 2.39×10^{-8} cal. per erg,

α = volume of the unit of flow per gram atom, cu. cm. (in terms of Kauzmann's constant, $\alpha = 6.023 \times 10^{23} qAL$)

n = number of atoms per unit of flow

V_0 = atomic volume

The following values of the characteristic constants for cold-drawn, annealed Monel were readily calculated from plots of the creep data:

$$Q = 37{,}200$$
$$\Delta\eta = -67.5$$
$$\Delta F = 37{,}200 + 67.5T$$
$$\gamma = 1.55 \times 10^{-9}$$
$$\alpha = 0.693T$$
$$n = 0.0926T$$
$$V_0 = 7.49$$

Values of n at the test temperature are given in Table 6 for comparison with similar data for cold-drawn, annealed Inconel.

TABLE 7.—*γ and n for Cold-drawn, Annealed Inconel*

Test Temperature, Deg. F.	γ	n
800	1.05×10^{-9}	42
900	1.05×10^{-9}	45
1000	1.55×10^{-9}	71
1100	2.20×10^{-9}	108

The creep constants for cold-drawn, annealed Inconel were not so readily determined, owing to the nature of the data. After a few trials a set of self-consistent plots, necessary for the calculation of the creep constants, was obtained, from which it was possible to calculate the creep constants given in Table 7.

TABLE 8.—*Comparative Working Stresses for Cold-drawn, Annealed Monel and Some Steels*[a]

POUNDS PER SQUARE INCH

Temperature, Deg. F.	750	800	850	900	950	1000	1100
Working stress:							
Cold-drawn, annealed Monel	16,800	12,400	8,800	6,300	4,150	2,900	
0.1 to 0.2 per cent carbon steel, p. 1, Sec. A, 8a		9,600		5,880			
0.1 to 0.2 per cent carbon steel, p. 1, Sec. A, 8b		6,000		4,400			
0.1 to 0.2 per cent carbon steel, p. 1, Sec. A, 3a		14,600		10,200		2,160	688
Carbon steel (0.20 per cent C max.), p. 225, Sec. F, 3		10,200				2,220	
1.0 to 2.5 per cent Cr, 0.50 per cent Mo steel (0.20 per cent C max.), p. 275, Sec. H 3c		17,600				4,550	
1.0 per cent Mo steel (0.20 per cent C max.), p. 405, Sec. N, 8b		20,100		9,450		4,520	
Ni-Mo steel, p. 445, Sec. Q, 3						3,720 500 hr.	
Cr-W-Va steel, p. 477, Sec. T, 2e				6,400[b] 500 hr.		2,880[b]	

[a] Working stress = 80 per cent of the stress to produce 0.01 per cent per creep per 1000 hours.
[b] Extrapolated.

The other values for cold-drawn, annealed Inconel are:

$$Q = 35{,}600$$
$$\Delta\eta = -66.6$$
$$\Delta F = 35{,}600 + 66.6T$$
$$V_0 = 6.75$$

Comparison of the data for the two alloys reveals little difference in the activation energy or entropy change for the creep process, the essential difference in the data being the temperature variation of γ for the cold-drawn, annealed Inconel.

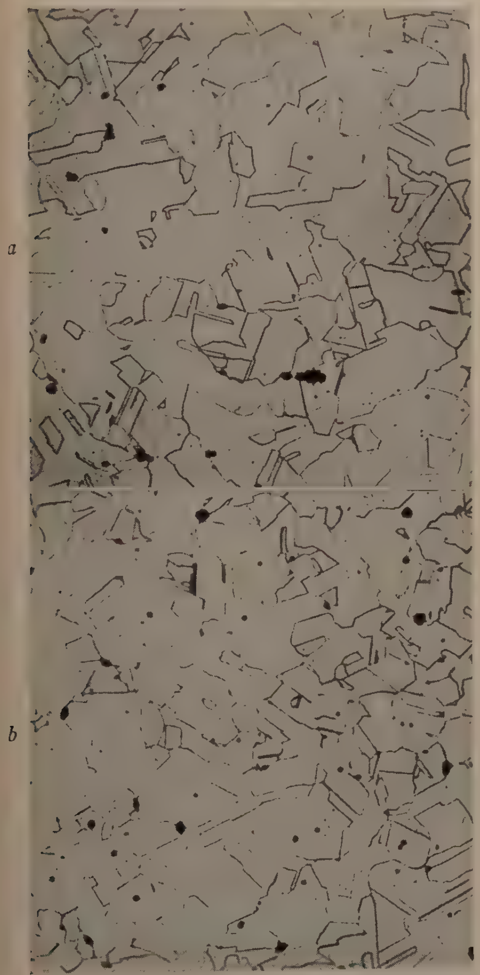

FIG. 9.—LONGITUDINAL SECTIONS OF COLD-DRAWN, ANNEALED MONEL BEFORE AND AFTER CREEP TESTING. × 100.

Etched in a one to one mixture of nitric and acetic acid.

a. Original material as annealed.

b. Microstructure after testing at 900°F. and 15,000 lb. per sq. in. for 2790 hours.

COMPARISON OF COLD-DRAWN, ANNEALED MONEL WITH SOME STEELS

As stated previously, Monel, in respect to its creep resistance, should be classed with steels. A comparison of the cold-drawn, annealed Monel creep-strength data with similar data on steels given in the "Compilation of Available High Temperature Creep Characteristics of Metals and Alloys," by the joint A.S.M.E.-A.S.T.M. committee in 1938, is given in Table 8. All stresses given are the working

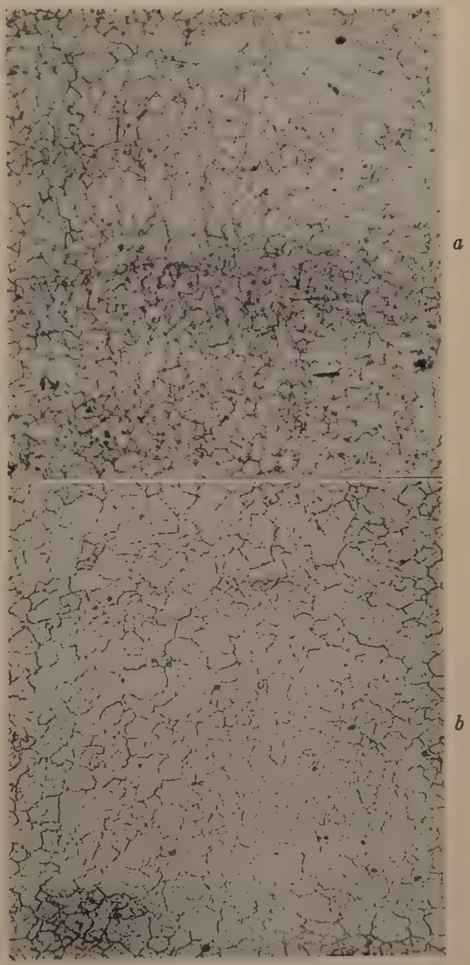

FIG. 10.—LONGITUDINAL SECTIONS OF COLD-DRAWN, ANNEALED INCONEL BEFORE AND AFTER CREEP TESTING. × 100.

Etched electrolytically in a 10 per cent solution of sulphuric acid.

a. Original material as annealed.

b. Microstructure after testing at 1100°F. and 5000 lb. per sq. in. for 1602 hours.

stresses for that temperature based on 80 per cent of the stress to produce 0.01 per cent creep per 1000 hr. as determined by laboratory test. This procedure is that followed by the Boiler Code Committee of the American Society of Mechanical Engineers in establishing working stresses for wrought ferrous materials at elevated temperatures. References to the steels are given with page number, section designation, and laboratory designation in the reference mentioned. It will be noted that cold-drawn, annealed Monel falls approximately at the mean of those steels considered.

Summary

Data have been presented on cold-drawn, annealed Monel and Inconel showing them to be suitable for use at elevated temperatures. The Inconel was found to have approximately twice the load-carrying capacity of Monel at all the test temperatures. However, Monel compares favorably in creep strength with many low-alloy steels and should not be classed with copper alloys, although it contains a large percentage of copper. Neither of the two alloys exhibited signs of stress-time embrittlement during the creep tests.

Acknowledgment

The authors wish to express their appreciation for the careful testing done by their associates, C. F. Crumbley and R. E. Crickmer, now in the United States Army, and to the International Nickel Co., Inc. for permission to publish these data.

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DISCUSSION

(E. E. Schumacher presiding)

H. L. Burghoff.*—Have the authors any information on the effect of grain size in these materials? There is a material difference in the grain sizes shown for the Monel and the Inconel. Is a wide range of grain size normally found for each material, and, if so, what is its effect upon creep strength?

H. L. Eiselstein.—The grain size for Monel shown in the micrograph is the usual size found in that product. The grain size of Inconel is about the same as that, too. However, we have run tests on Inconel at higher temperatures than those reported in this paper, and have found that the coarser grain size has a better creep resistance; and that the grain size that gives the best creep resistance at 1600°F. is about 0.005 in. in diameter. We have no test on Monel with varying grain size.

J. J. Kanter.†—It has been known for a long time that Monel metal exhibits ductility anomalies at elevated temperatures. Even in short-time test, it can be demonstrated in the range of 900°F. that there is a distinct falling off of the ability of Monel metal to elongate, and in rupture tests this shortcoming is still further accentuated. Knowledge of this rupture anomaly of Monel metal may be one of the reasons for which designer's approach certain high-temperature applications with reservations.

The authors of this paper have merely demonstrated that for 900°F. the alloy has an ability to elongate 1.7 per cent over a period of some 2700 hr. Before any conviction can be expected from designers that Monel metal is applicable to stress design in such range of temperature, I think it is desirable to demonstrate the capacity for the material to elongate over a longer period of time than has been done in this presentation.

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† Crane Co., Chicago, Illinois.

H. L. Eiselstein.—We do not have any rupture data on Monel at any temperature. However, we do have considerable rupture data on Inconel at 1000, 1200, 1400 and 1600°F., and considerable ductility is shown at all those temperatures. The elongations at fracture are from 50 to 100 per cent, but we have no data on Monel.

A. I. Blank.*—The authors are to be congratulated for a very fine paper and the presentation of some urgently needed creep data on nickel alloys.

This is the second of two papers in this symposium that may have given the impression that the relationship between stress and creep rate developed by Nadai and McVetty is not favorably considered. It is my belief, however, that this impression was not intended. The contributions of Nadai and McVetty to interpretation of creep data have provided a highly applicable, mathematical expression for the rate at which metal under stress will flow at elevated temperature. Although experimental results deviate in many instances from values calculated by this method, it is nevertheless very useful where only limited experimental data are available.

R. B. Gordon.†—I think too much emphasis can be placed upon minimum creep rate. Most designs that engineers are concerned with are limited by the amount of permissible creep. It is fortunate that the authors did put in a few of their original creep curves. An example of what I mean is shown by Fig. 2. After Inconel, at 40,000 lb. per sq. in., has reached a steady creep rate, it creeps only about 0.6 per cent in 1000 hr. However, when the load is applied it stretches 3 per cent. In other words, the minimum creep rate for the 40,000-lb. test will give an engineer no useful information where he has a design with one per cent permissible creep.

Another thing I would like to comment upon is the utility of impact tests or tensile tests made at room temperature after test in evaluating embrittlement at service temperatures. Are materials in service at elevated temperatures often subjected to conditions in which they fail at room temperature? I feel that we are really interested in something along the lines Mr. Kanter has been talking about; namely, a test made at test temperature.

We have been carrying out some experiments along this line in which we raise the load at the end of a creep test and conduct a short-time creep-rupture test. For this purpose, we are fortunate in having a new type of creep-testing apparatus in which we can make accurate tests in the creep range as well as in the rupture range and obtain an autographic curve. In our opinion, the ductility obtained on a rupture test at test temperature is more valuable than the results of room-temperature tests.

H. L. Eiselstein.—The data necessary for computing total strain at any given time are in the paper. McVetty's equation for total creep is given, and also the necessary constants and figures.

Raising the stress on the specimen after the creep test has been tried in our laboratories on other alloys that come under the orders of secrecy, but the data we have give no good indication of the ductility of the material.

J. J. Kanter.—The authors have taken the trouble to compute some constants according to the theory that was advanced by Kauzmann and elaborated upon later by Dushman. According to Kauzmann's conception, there must be a little block of atoms energized before creep can take place, and that little block is represented by the constant N. According to the data from which this constant has been calculated, it increases in size as the temperature increases. I wonder whether the authors have given any thought to rationalizing that fact? Intuitively, I should say the size of that block of atoms ought to decrease rather than increase as the temperature goes up.

H. L. Eiselstein.—What Mr. Kanter has mentioned has been explained excellently by G. I. Taylor in the *Proceedings* of the Royal Society along about 1937.

We have other data showing the size of the unit of flow as increasing with increasing temperature on an age-hardenable alloy, and it is quite easily explained there by the fact that the materials were overaged, making it possible for a large line dislocation of the type postulated by Mr. Taylor.

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In Taylor's original article on the theory of dislocations, the increase in size of the line—what he calls a line dislocation—is explained by the fact that at higher temperatures there are in the mosaic structure of the crystal fewer lines of distribution registry, making it possible for the dislocation to propagate itself or grow without crossing a boundary—more lines of registry between the mosaic blocks. That was his original hypothesis and he has written a rather lengthy article on the subject.

W. E. KINGSTON.*—It might not be out of place to indicate some of the creep problems that those of us in the radio industry encounter. This is particularly true in the application of various alloys to radio-tube filaments. In the nickel-base alloys, which operate at a temperature between 700° and 900°C., and where, in order to prevent vibration or microfinism, stresses in the order of about 6000 lb. per sq. in. must be placed on the filament. Of course, at these temperatures, which are considerably above the equicohesive or recrystallization temperature of the alloy, characteristic high-temperature creep failures occur. These invariably show up as ruptures at the grain boundaries.

We are limited in our work by the fact that we have other physical properties to consider, such as the electrical resistivity of the alloy, which must be held within very close limits, and the filament diameter, which must be maintained close to an optimum size, since it must operate at a specified temperature with a definite power input. These and other restrictions tend to limit the nature of the constituents that we can utilize in alloys for this purpose.

In brief, our work has been concentrated along the lines of the development of alloys whose recrystallization or equicohesive temperature is above the temperature at which these filaments operate; in other words, alloys having a recrystallization temperature in the order of 1000°C. Such alloys, when operated under the equicohesive temperature, say perhaps at 800°C., exhibit very low creep values.

We have been fortunate in being able to develop a series of alloys that have the properties we desire, and we have made a very comprehensive study of these alloys. Creep analyses are made at the actual diameter of the wire as it is used in a radio-tube filament. This means that the specimens are in the order of less than one-thousandth of an inch in diameter, so it is evident that the technique used in such analyses must be quite different from that for conventional creep measurements.

H. L. EISELSTEIN.—I believe that in an article in the bibliography in the *Journal of Applied Physics*, 1944, Dushman, Dunbar and Hutsteiner told of performing tests on fine wires at high temperatures. Possibly some of their creep-testing technique would be of interest.

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* Sylvania Electric Products Inc., Bayside, N. Y.

Properties of Some Cast Copper-base Alloys at Elevated Temperatures

By H. E. Montgomery*

(Cleveland Meeting, October 1944)

Engineering trends for some years have been toward higher temperatures, both in process work and in steam generation. Progress in design has been dependent upon the development and evaluation of suitable alloys. Elementary knowledge of the limitations of copper-base alloys indicate their unsuitability for the higher ranges of operating temperatures; say, for steam to 950°F.

Emphasis upon the more severe conditions perhaps is a reason why more complete evaluations have not been made for copper-base alloys over their range of suitability. However, the few studies made show clearly the need for more accurate evaluations. Some copper-base alloys long looked upon favorably because of superior room-temperature properties are not as desirable as some others perhaps not so "strong" and "hard," as measured by usual acceptance tests.

Load-carrying capacity and structural stability are two important factors. Structural stability as influenced by temperature, by presence of corrosive media, or by the effects of stress itself, frequently is a limiting factor.

An early reference to creep properties of the cast copper-base alloys is that of Brown[1] (Admiralty gun metal, Cu 87.5, Sn 10.1, Zn 2.3 and Pb 0.08). His tests were similar to present-day stress-rupture tests without measurement of creep elongation. Loading was in steps with usually 24 hr. between steps, and continued until failure. He advocated a "useful strength value" of 6½ tons (14,560 lb.) per sq. in. at 572°F. (300°C.). A specimen broken in ½ hr. at 572°F. had a strength of 21 tons (26,880 lb.) per sq. in. The strength values as determined by ½-hr. tests and those by the longer stress-rupture start to differentiate at 392°F. (200°C). This is the temperature at which time at load began to play an important part.

Bolton, Price and Hebemann[2] give creep curves on 88-10-2 (A.S.T.M. B-60, Cu 88, Sn 10, Zn 2) and steam or valve bronze (A.S.T.M. B-61, Cu 87.50, Sn 6.00, Zn 3.75, Pb 1.70) at 500°F. Direct comparison of the two alloys under 7500 lb. per sq. in. stress showed the steam bronze (A.S.T.M. B-61) superior in creep strength to the 88-10-2 (A.S.T.M. B-60). The steam bronze shows no creep after 700 hr. (1540-hr. test). The 88-10-2 shows a rate of about 7.0 per cent in 100,000 hr. over the last 700 hr. of the test. Creep curves on the steam bronze are also given at the same temperature (500°F.) with loads of 6500 lb. per sq. in. and 8000 lb. per sq. in. These indicate "creep strengths" (creep rate within 1 per cent in 100,000 hr.) in excess of 8000 lb. per sq. in. for this alloy.

It was found that higher percentages of tin are detrimental to creep resistance. This is caused by the presence of or formation during test of considerable alpha-delta eutectoid in the higher tin alloys. Bolton also states that the high

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[1] References are at the end of the paper.

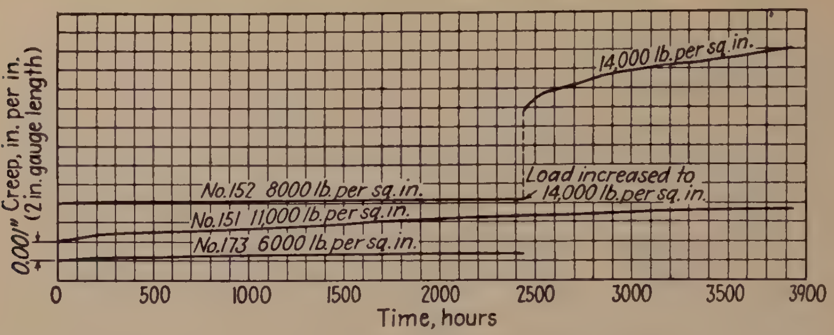

FIG. 1.—CREEP CURVES ON 85-5-5-5 AND 88-10-2 AT 450°F.

No.	Composition, Per Cent				Physical Properties					
					Before Creep			After Creep		
	Cu	Sn	Zn	Pb	Ult. Strength, Lb. per Sq. In.	Elongation, Per Cent	RWL E	Ult. Strength, Lb. per Sq. In.	Elongation, Per Cent	RWL E
151	84.84	5.09	4.75	4.77	38,400	30.1	64	31,200	15.8	69
152	84.84	5.09	4.75	4.77	38,400	30.1	64	27,800	9.7	68
173	87.44	9.00	2.80	0.05	48,500	55.9	65	31,300	12.2	66

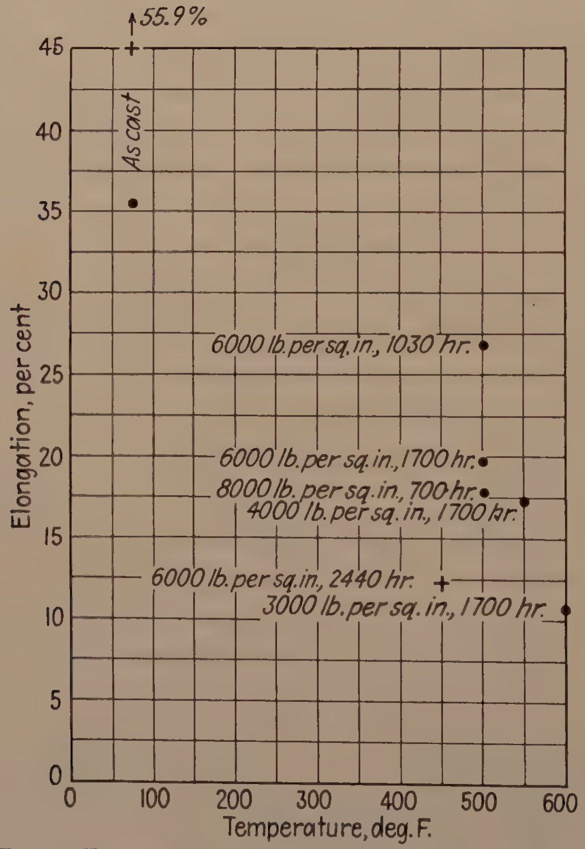

FIG. 2.—ELONGATION OF 88-10-2 (B-62) AFTER CREEP TESTING.

zinc-copper-base alloys have poor creep resistance at comparatively low temperatures.

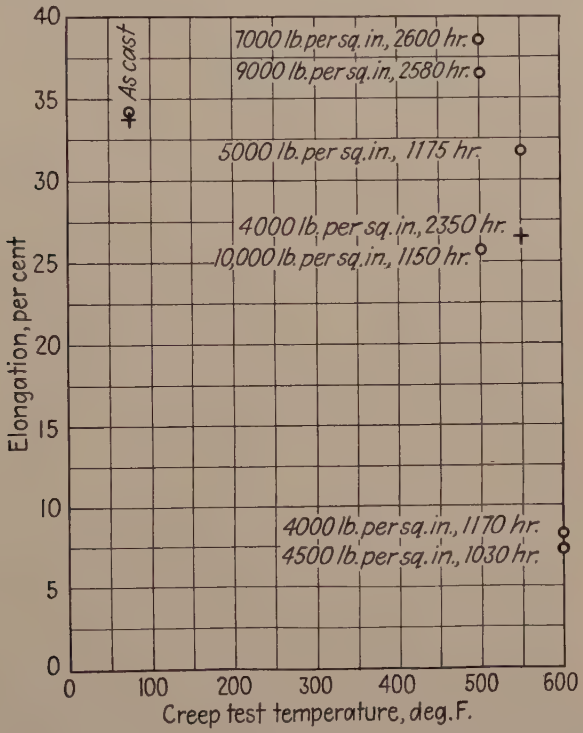

FIG. 3.—ELONGATION OF STEAM BRONZE (B-61) AFTER CREEP TESTING.

Kanter[3] gives creep curves on 85-5-5-5 (A.S.T.M. B-62, Cu 85.0, Sn 5.00, Zn 5.00, Pb 5.00) alloy at 500°F. and 4000 and 5000 lb. per sq. in. His curves (limited to 700 and 750 hr.) indicate that the alloy has a "creep strength" (creep rate within 1 per cent in 100,000 hr.) in excess of 5000 lb. per sq. in. Tabular data on a copper-aluminum (91½–7½) die-cast bronze shows a load of 10,000 lb. per sq. in. sustained at 560°F. with an extension within 1 per cent in 10,000 hr. At 845°F., 3000 lb. per sq. in. is sustained. Kanter confirms Bolton's statement regarding the alloys with high zinc content. Creep-strength curves based on 1 per cent extension in 10,000 hr. are given for a cast bronze (Crane "hard metal," Cu 88, Sn 12) and a cast red brass (Cu 86, Sn 6, Zn 5 and Pb 2).

Kanter states that although the cast bronze shows better tensile strength and proportional limit throughout the temperature range to 800°F. the cast red brass has better creep properties at temperatures above about 450°F. Structural breakdown of the cast bronze of higher tin content at the higher temperatures is stated as the probable cause of this.

Bolton[4] shows creep-test results on 88-10-2 and valve or steam bronze. Tabulated creep results are given in Table 1. Table 2 shows results of tensile tests after removal from creep test.

In comparing 88-10-2 and steam bronze alloys, Bolton says there should be no hesitancy in specifying steam bronze alloy for stresses within those required to produce 0.1 per cent creep in 10,000 hr. at 500°F. and probably even at 550°F.

TABLE 1.—*Creep on A.S.T.M. B-60 and B-61*

Alloy	Specimen	Temperature, Deg. F.	Load, Lb. per Sq. In.	Rate, Per Cent in 10,000 Hr.
88-10-2 (A.S.T.M. B-60)	B	500	6,000	0.29[a]
	D	550	4,000	0.20[a]
	E	600	3,000	0.45[a]
Valve bronze (A.S.T.M. B-61)	A	500	7,000	nil[b]
	B	500	9,000	0.18
	C	500	10,000	1.00
	D	550	5,000	0.28
	E	600	4,000	1.77

[a] Rate based on last 1200 hr. of 1700-hr. tests.
[b] Rate based on test beyond first 500 hours.

However, 88-10-2 alloy should be limited to 450°F. and low design stresses. It is shown that the 88-10-2 alloy particularly shows structural breakdown, precipitation of alpha-delta eutectoid in grain-boundary positions causing embrittlement. Bolton suggested that an excess of solute is responsible and that in the steam-bronze type itself the maximum tin should be restricted to 6.5 per cent. This was done later in both governmental and engineering society specifications for this alloy.[5] The phenomenon (grain-boundary precipitation) is essentially an "age-hardening" one. It is interesting to note that stress as well as degree of supersaturation contributes to the rate of precipitation.

TABLE 2.—*Tensile Tests*

Alloy	Specimen	Temperature, Deg. F.	Creep Load, Lb. per Sq. In.	Duration, Hr.	Elongation, in. 2 In., Per Cent	Tensile Strength, Lb. per Sq. In.
88-10-2 (A.S.T.M. B-60)	Original		None		35.4	49,100
	A	500	6,000	1,030	26.7	43,200
	B	500	6,000	1,700	19.8	39,400
	C	500	8,000	700	17.6	38,900
	D	550	4,000	1,700	17.2	38,000
	E	600	3,000	1,700	10.7	33,300
Valve bronze (A.S.T.M. B-61)	Original		None		34.3	37,800
	A	500	6,000–7,000[a]	2,100	38.7	37,750
	B	500	8,000–9,000	2,100	36.7	38,000
	C	500	10,000	1,150	25.8	31,800
	D	550	5,000	1,180	31.8	33,200
	E	600	4,000	1,180	8.1	17,000

[a] Step loading.

Table 3 shows some data on creep-strength properties published by W. C. Stewart[6] on gun metal.

The A.S.T.M.-A.S.M.E. Creep Data Book[7] gives data submitted by two cooperators. Laboratory No. 2 submitted creep data on manganese bronze (Cu 57, Sn 0.10, Zn 40, Pb 0.49, Al 0.44, Fe 1.72), 85-5-5-5 (A.S.T.M. B-62), valve bronze (A.S.T.M. B-61), hard bronze (Cu 86.21, Zn 1.46, Sn 12.25) and aluminum bronze (Cu 91.47, Sn 0.8, Al 7.68, Fe 0.66, P 0.01) alloys. Short-time tensile-test results before creep are given for all except the 85-5-5-5 alloy. Results in tabular form are given in Table 4. Rockwell tests before and after creep tests show higher hardness values after testing (cast manganese bronze excepted). This indicates a structural change.

TABLE 3.—*Creep Properties of Gun Metal*[6]

Material	Temperature, Deg. F.	Stress (Lb. per Sq. In.) to Produce Creep Rate of	
		0.01 Per Cent per 1000 Hr.	0.1 Per Cent per 1000 Hr.
88-10-2 (A.S.T.M. B-60)	400	10,000	14,000
	500	5,400	8,000
	600	2,600	4,000
90-6-2-2	400	8,000	12,000
	500	5,400	8,000
	600	2,800	3,600

Laboratory No 19 has submitted data on steam bronze (A.S.T.M. B-61), 88-10-2 (A.S.T.M. B-60) and 85-5-5-5 (A.S.T.M. B-62) alloys.

TABLE 4.—*Creep Data on Cast Nonferrous Alloys*[a]

Materials Designation	Material	Temperature, Deg. F.	Load, Lb. per Sq. In.	Hours	Rate, Per Cent per 1000 Hr.
2a	Manganese bronze	300	10,000	500	0.118
		350	10,000	500	0.069
2b	85-5-5-5	500	3,000	3,000	0.028
		500	3,000	1,000	0.018
		500	10,000	1,000	0.085
		500	10,000	4,000	1.250
2c	Valve bronze	500	10,000	250	0.096
		550	10,000	750	1.33
		600	2,000	500	0.052
		600	1,000	500	0.042
		600	3,000	250	0.108
		700	3,000	500	0.650
2d	Valve bronze	400	10,000	250	0.015
2e	Hard bronze	500	10,000	250	0.026
		550	3,000	250	0.104
		600	2,000	500	0.080
2f	Hard bronze	450	10,000	250	0.035
		500	10,000	250	0.185
		550	10,000	500	4.60
		600	3,000	250	0.056
		650	3,000	250	0.30
		700	3,000	250	0.41
2g	Aluminum bronze	600	10,000	500	0.54
		800	3,000	250	0.038
		900	3,000	250	0.35
19*a*	Valve bronze	550	4,000	2,350	0.015
19*e*	Valve bronze	Room	8,000	1,800	nil
		Room	12,000	1,520	nil
		Room	14,000	1,780	nil
19*f*	Valve bronze	600	3,000	530	nil
		Step load	4,500	470	0.10
		500	6,000	250	nil
19*g*	85-5-5-5	500	6,000	1,180	nil
		500	6,000	1,700	nil (last 850 hr.)
		500	8,000	1,500	0.019
19*h*	85-5-5-5	500	4,500	2,016	nil
		Step load	7,000	484	0.005
		500	6,500	2,400	0.015

Materials Designation	Material	Before Ultimate Strength		After Ultimate Strength		Hours under Test	Temperature, Deg. F.	Load, Lb. per Sq. In.
		Lb. per Sq. In.	Elongation Per Cent in 2-in. Gauge	Lb. per Sq. In.	Elongation, er Cent in 2-in. Gauge			
19*a*	Steam bronze	40,000	34.0	43,900	26.5	2,350	550	4,000
19*f*	Steam bronze	37,800	34.5	20,800	7.5	1,030	600	3,500 4,500
19*g*	85-5-5-5	30,200	23.8	29,400	18.3	1,700	500	6,000
		30,200	23.8	31,750	29.0	1,180	500	6,000
		30,200	23.8	31,000	23.2	1,700	500	8,000
19*h*	85-5-5-5 (contains 0.82 % Ni)	36,800	32.9	33,500	13.5	2,500	500	4,500 7,000
		36,800	32.9	36,500	19.9	2,400	500	6,500

[a] Taken from 1938 A.S.T.M–A.S.M.E. Creep Book, Cooperators 2 and 19.[7]

Table 4 includes room-temperature tensile-test properties before and after creep test on specimens 19*a* and 19*f*.

Fig. 1 shows two creep curves on 85-5-5-5 alloy and one on 88-10-2, which have been run during the past year in the Lunkenheimer Company's laboratories. Creep rates and before and after creep-test tensile properties are given in Table 5. These tests were made on specimens sand-cast approximately to size with gating very similar to A.S.T.M. EA-B61-42, Fig. 4.

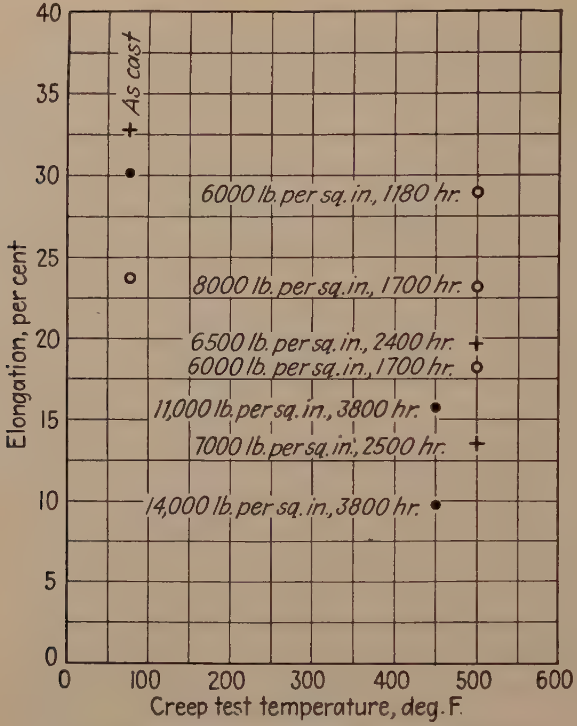

FIG. 4.—ELONGATION OF 85-5-5-5 AFTER CREEP TESTING.

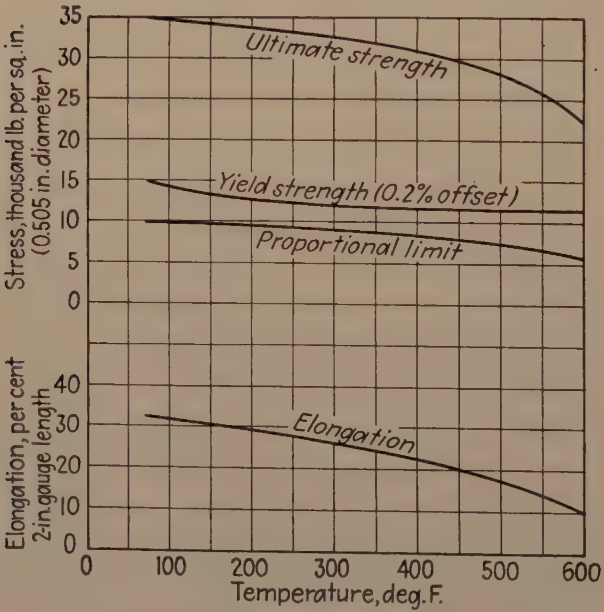

FIG. 5.—EFFECT OF TEMPERATURE ON 85-5-5-5.

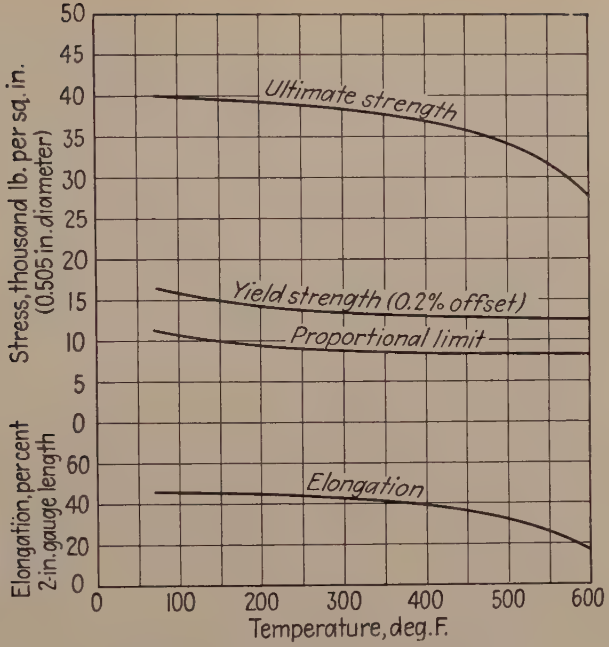

Fig. 6.—Effect of temperature on steam bronze.

A specimen 0.505-in. diameter by 2-in. gauge length was used. All tests were made in accordance with A.S.T.M. Specification E-22-41, Recommended Practice for Conducting Long-time High-temperature Tension Tests of Metallic Materials. These tests indicate that the maximum permissible operating temperature for these alloys should be no greater than 450°F. with stresses kept low. These results corroborate the observation that higher loads increase structural breakdown tendency.

Table 5.—*Creep Data on* 85-5-5-5 *and* 88-10-2

Material	Creep-test Load, Lb. per Sq. In.	Temperature of of Test, Deg. F.	Hours at Test	Creep Rate, Per Cent in 10,000 Hr. over Last 1000 Hrs. of Test
85-5-5-5	8,000	450	2,440	0.05
85-5-5-5	14,000[a]	450	1,390	1.3[b]
85-5-5-5	11,000	450	3,830	0.3
88-10-2	6,000	450	2,440	0.05

Physical Properties

Material	Creep Load, Lb. per Sq. In.	Before Creep		After Creep	
		Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent
85-5-5-5	14,000	38,400	30.1	27,800	9.7
85-5-5-5	11,000	38,400	30.1	31,200	15.8
88-10-2	6,000	48,500	55.9	31,300	12.2

[a] Step test.
[b] Over last 800 hr.

In Figs. 2, 3 and 4 are plotted the values of elongation on 88-10-2, steam bronze and 85-5-5-5 alloys after creep testing at various temperatures. Original room-temperature elongation values are included. Definite trends are shown in the relative ability of the various alloys to resist embrittlement under stress at the higher temperatures for various time periods.

Figs. 5, 6 and 7 show the effect of temperature on the short-time tensile properties of the same alloys. These tests were made on individually cast specimens as shown in Specification EA-B61-42,

Fig. 4. All tests were made in accordance with A.S.T.M. Specification E-21-42T, Recommended Practice for Short-time Elevated-temperature Tension Tests of Metallic Materials (Tentative). These curves show that the 88-10-2 (A.S.T.M. B-60) is stronger under short time loading than steam bronze (A.S.T.M. B-61).

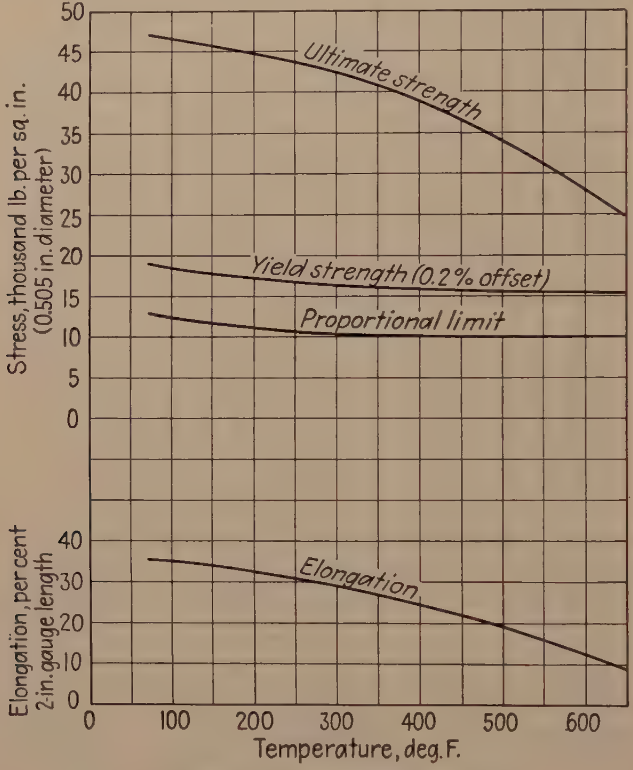

Fig. 7.—Effect of temperature on 88-10-2.

Conclusion

A survey of the experimental data indicates that temperature, stress, and time affect the structural stability of the materials, as evidenced by loss of ductility or increase in hardness. At a given temperature where structural deterioration occurs it is hastened by higher stresses and the amount depends upon the exposure time. The data show that some alloys have higher short-time tensile strength at elevated temperatures but lose this favorable position when exposed to temperature and stress for long periods of time.

In general, to avoid excessive loss in ductility due to structural deterioration, the operating temperature should not exceed 425°F. for 85-5-5-5, 450°F. for 88-10-2 and 550°F. for steam bronze, and the stress at these temperatures should not exceed the stress giving a creep rate of 0.1 per cent in 10,000 hr. The available data would indicate creep strengths (to give 0.1 per cent in 10,000 hr.) of 8,500 lb. per sq. in. for 85-5-5-5 at 425°F., 6000 to 6500 lb. per sq. in. for 88-10-2 at 450°F., and 3800 to 4000 lb. per sq. in. for steam bronze at 550°F. In the use of these materials all the variables, stress, temperature and time must be taken into consideration. With lower stresses and short exposure periods the operating temperature may be increased, and, conversely, when service time or stress is increased the operating temperature must be reduced.

The foregoing résumé gives a fairly complete review of what has been published on the high-temperature creep properties of the cast nonferrous copper-base alloys. The paucity of data emphasizes the need for further studies.

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DISCUSSION

(*E. E. Schumacher presiding*)

A. J. Smith.*—Certain things have come up in the earlier papers which have a bearing on this present paper. Mr. Kanter spoke of cataclysmic failure. Many of the bronzes, especially in the casting varieties, are not single phased, although some of them, such as the steam bronze mentioned, are within the alpha solubility limit over the whole working range. The manganese bronzes and others of that type normally have a second phase present and usually a diminishing solubility on approaching room temperature. The normal casting at room temperature may be thought to have a quasistability. However, when the temperature is raised precipitation takes place and this complicates the making of creep studies on the material.

This is true of the alloys 85-5-5-5, leaded red brass, and 88-10-2, gun metal, in which the delta phase coexists with the alpha over the normal operating temperatures and the limiting temperature for service is set not only by the creep behavior of the material but also by deterioration due to precipitation. The delta rejected from the alpha invariably comes out on the grain boundaries, embrittling the material. In many cases of this sort, where the material is initially ductile it flies to pieces in a hurry when the grain boundaries become loaded with precipitate, and the action can become what Mr. Kanter described as cataclysmic failure.

From the structural point of view, these alloys must be treated a little differently from the worked alloys discussed earlier. Cold-worked and annealed alloys lying wholly within a single-phase region do not possess a complete structural stability. In the cast alloys, however, there is relatively little change at elevated temperature from recrystallization and grain growth since no working is usually performed on them.

(*H. L. Burghoff presiding*)

H. L. Burghoff.*—I have a question, Dr. Smith. A number of the alloys you mentioned contain lead, which, of course, is present as discrete particles. At what level of concentration does lead begin to play an important part in determining these elevated-temperature characteristics?

A. J. Smith.—That is a difficult question to answer because of the complicating features of the alloys that are lead free. I do not know of any work done on the subject. But for comparison, 85-5-5-5 has about the same characteristics at, say 450°F. as 88-10-2, which is lead free or contains at most 0.30 per cent. Both 85-5-5-5 and 88-10-2 precipitate delta. The specification limit of usage is 406°F., temperature of saturated steam at

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* Lunkenheimer Company, Cincinnati, Ohio.

* Chase Brass and Copper Co., Waterbury, Connecticut.

250 lb. per sq. in. gauge pressure, and the larger portion of these materials would go into pressure-containing parts for such service; 406°F. is just about the safe limit for both alloys, in spite of the 5 per cent lead in 85-5-5-5.

A. I. Blank.*—It is possible that a closer approach to service conditions might be obtained by preheating these materials for a considerable period of time before the creep tests are begun. A condition of greater stability during the tests would be effected by previous precipitation of virtually all phases. It would be interesting to learn whether any work has been done along this line.

A. J. Smith.—That would be to suggest using, say, 85-5-5-5, which would show no precipitation below 450°F. or somewhat under that, and using it at a higher temperature, say 500°F., after the delta has precipitated. No work has been done of that sort that I know of, and considering the rigidity of the code specifications, I think that even though we had data on the point, we could never secure acceptance of such a practice, and that it would be of more theoretical than practical interest.

I will make the further point, that no matter what we do in any heat-treatment, and many have been tried, not for carrying out creep studies afterward but merely to give a certain structural stability for ordinary purposes, we cannot take the delta out of the grain boundaries. When it gets in there, the elongation, which might run 35 per cent or more, is dropped to 1 or 2 per cent, or even less sometimes.

J. S. Roberts.†—Is there any relationship between tensile strength and creep properties; that is, as the tensile strength goes up, do the creep properties improve?

A. J. Smith.—Of the two materials cited, the gun metal, of 10 per cent tin and 2 per cent zinc, has higher room-temperature properties than the steam bronze of about 6 per cent tin, 4 per cent zinc and 1.5 per cent lead. In good foundry practice the gun metal might run well in excess of 45,000 lb. tensile strength and should run around 50 per cent elongation or better. The steam bronze will run around 40,000 lb. tensile strength and 40 per cent elongation. However, the gun metal gives out rather rapidly between 450° and 500°F. Steam bronze is good indefinitely at 550°F. with normal stresses, its rated temperature. Precipitation of delta accounts for part of the difference between these two materials and not the creep strength alone. Precipitation always causes difficulty in interpreting creep data for these materials.

P. A. Beck.*—Is there any effect of the grain size in preferred orientation in these materials in the creep strength?

A. J. Smith.—I do not believe any investigation has been made on that. By and large, all of the creep tests have been run on bars cast roughly to size, in which if the A.S.T.M. pattern, for example, were followed with heavy over-all riser the length of the bar, there would be a marked directional orientation of the grains, whereas in our own practice with risers on each end making the entire bar sand-covered, the usual dendritic pattern for a round bar is found; yet comparative tests on the two bars give approximately the same results in elevated-temperature testing. Do you know anything about that, Mr. Halliwell?

G. P. Halliwell.†—What type of test bar was used, Lunkenheimer or Webbert?

A. J. Smith.—Both bars were used but the elevated-temperature bar recommended by the A.S.T.M. is longer than the regular room-temperature bar; that is, the bar is cast for threaded ends about 7 in. long and a somewhat longer gauge length for uniform temperature distribution. The bar can be made with a Webbert gate but in our practice we are casting it in the same way as the Lunkenheimer bar, with a riser at each end. There is quite a difference in the orientation effect, using the different types.

G. P. Halliwell.—Yes, there would be a difference in the dendritic crystal formation of the two bars. I am interested, however, in knowing whether you have noticed in high-temperature creep tests any propensity of the Webbert bars to break in or near the shoulders, as compared with the Lunkenheimer bar, which apparently is less prone to fracture in this manner at room temperature.

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* Chase Brass and Copper Co., Waterbury, Connecticut.

† American Manganese Bronze Co., Philadelphia, Pennsylvania.

* Cleveland Graphite Bronze Co., Cleveland, Ohio.

† H. Kramer and Co., Chicago, Illinois.

A. J. Smith.—The elevated-temperature bar is made somewhat differently, in that it has a stepped-off section and a much greater radius. In our elevated-temperature bar, the stepped-off section is much longer—1⅛ in. in the A.S.T.M. bar. The reduced section of our own bar is 3 in. long. With the greater length of the stepped-off section, there is more of a tendency for the Webbert bar to break within the gauge instead of breaking at the reduced end, as it normally does in the room-temperature bar.

Creep Data on Die-cast Zinc Alloy

By E. H. Kelton* and B. D. Grissinger*

(Cleveland Meeting, October 1944)

In designing structural members of steel and some other materials the design engineer has available recognized values of elastic modulus and safe working stress that may be substituted in well-known engineering formulas to give him desired cross-sectional areas and deflections for a particular part.

Zinc, on the other hand, has no generally recognized modulus. It flows under continuously applied loads. Therefore, the designer of structural members must use a range of working stresses depending on the continuous load and the amount of permissible distortion. The only method of obtaining these values is by creep testing.

Creep testing of zinc has been carried on for some 20 years by this laboratory, covering a wide range of zinc and zinc alloys. Types of test included tension, compression, and simple and cantilever beams at temperatures ranging from 0 to 150°C. Specimen conditions ranged from as-cast or as-rolled to accelerated aged in steam or dry air. Effects of plating were investigated also. It is not the intention of this paper to expound all these factors but rather to present the final data on well-known zinc die-casting alloys and to suggest means of applying these data to engineering design.

EARLY WORK

In the early work on creep testing of zinc, the direct-loading tension method was used. However, direct loading of die castings was unsatisfactory because of the high loads required. For instance, a standard die-cast tension bar having a cross-sectional area of about 0.049 sq. in. would require a direct load of about 1000 lb. for a unit stress of 20,000 lb. per sq. in. Also, tests were made at nominal room temperature, but normal variations caused fluctuations greater than those due to experimental error or other causes, so that control of this variable within ±½°C. seemed essential. These two factors led to the development of an apparatus described by J. Ruzicka,[1] in which the specimens were loaded by means of a lever and were held at constant temperature by means of an oil bath.

While Ruzicka's apparatus yielded excellent check results, it seemed desirable to have some setup by which literally hundreds of die-cast specimens could be tested at the same time. This would permit the conducting of a number of low-load tests designed to run 10 years or longer and still leave capacity for current high-load work. Beam testing in a constant-temperature room was the answer.

TEST METHOD

Preliminary work indicated that die-cast beams of various lengths and cross sections yielded the same result within reasonable limits regardless of whether they were tested as simple beams, uniformly loaded beams, or cantilevers. Accordingly, the simplest type was adopted. This was a

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* Development Engineering Division, Technical Department, The New Jersey Zinc Company (of Pa.), Palmerton, Pennsylvania.

[1] References are at the end of the paper.

nominal ¼ by ¼ by 6-in. die-cast impact bar loaded by means of a yoke to provide uniform stress throughout a 3-in. section. Adapters were fitted to the ends of the beam to extend the effective length to 9 in. and thus reduce the loads required. The beams were supported by small rollers. The test setup is shown in Fig. 1.

The required load was calculated directly from the initial stress desired.

The deflection was measured by means of an Ames dial set into a yoke that spanned 2 in. of the uniformly loaded section. Since a uniformly loaded beam will deform in the arc of a circle in the early stages of deformation, it was feasible to calculate the percentage of elongation directly from the measured deflection.* Ordinarily tests were run up to about 3.5 per cent elongation.

Tests results were plotted in the form of log-elongation versus log-time graphs as shown in Fig. 2. This graph shows a typical series of tests on A.S.T.M. Alloy No. XXIII† at 25°C. with one, two, or three specimens at indicated loads varying from 2,500 to 25,000 lb. per sq. in. Graphs in this form (provided they include enough tests at a given load to indicate the range of deflections that may be expected) are perfectly satisfactory for use by design engineers. However, a more desirable form would present load versus log elongation with curves for various times ranging from instantaneous to 10 years. A plot of this type is shown in Fig. 3. The method of using this graph follows: Determine the per cent elongation* that is permissible

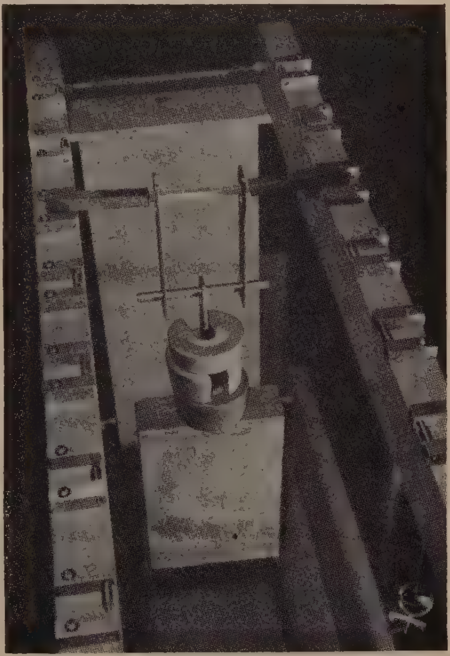

FIG. 1.—YOKE-LOADED BEAM CREEP TEST.

$$* \text{ Unit Strain } (e) = \frac{4dt}{4dt + 4d^2 + L^2}$$

Where L = length of beam on which deflection is measured,
d = deflection in length L,
t = thickness of test beam,

or since $t = 0.251$ in. and $L = 2$ in. in the ordinary test:

$$\text{Strain in 2 in. } (E) = \frac{0.502d}{1 + 0.251d + d^2}$$

† A.S.T.M. Specification B86-43:

Element, Per Cent	Alloy No. XXI	Alloy No. XXIII	Alloy No. XXV
Copper.........	2.5 to 3.5	0.10 max.	0.75 to 1.25
Aluminum......	3.5 to 4.5	3.5 to 4.3	3.5 to 4.3
Magnesium.....	0.02 to 0.10	0.03 to 0.08	0.03 to 0.08
Iron, max......	0.100	0.100	0.100
Lead, max......	0.007	0.007	0.007
Cadmium, max.	0.005	0.005	0.005
Tin, max.......	0.005	0.005	0.005
Zinc...........	remainder	remainder	remainder

* In applications involving beams the following approximate formulas have been found useful in determining the relations between the deflection and the elongation in the outer fiber of such members:

1. For cantilever beams $e = \frac{150dt}{L^2}$

2. For simple beams (concentrated load) $e = \frac{600dt}{L^2}$

where e = per cent elongation in outer fiber of the beam,
d = deflection of the beam, in.,
t = thickness of the beam, in.,
L = length of beam, in.

in the particular beam member in some particular time, say, for instance, five years. Find this per cent elongation on the ordinate and move horizontally across the chart until the chosen time curve is intercepted. From this point, move vertically down to the abscissa, which will indicate the permissible stress. For ordinary applications a factor of safety of 20 per cent is usually applied. Thus, if the permissible stress for the particular application is 2500 lb., the cross section would be designed to yield a stress of not more than 2000 pounds.

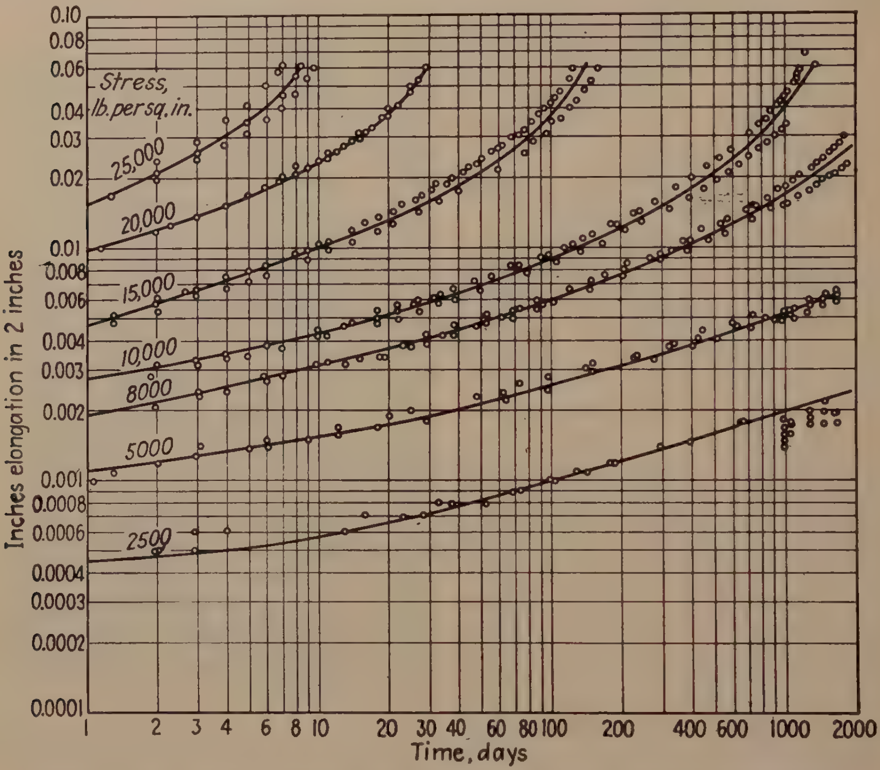

FIG. 2.—BEAM CREEP TESTS OF ALLOY NO. XXIII AT 25°C. AT VARIOUS STRESSES.

The graph also shows curves of pseudo-modulus. These are not true elastic moduli but the instantaneous moduli calculated from the stress-strain curves of Fig. 3 at any particular time. These values have been found useful in engineering calculations. They may be used in standard engineering formulas in place of the true modulus provided that it is understood that the value applies only for one particular load and one particular time at the temperature specified.

Fig. 3 contains a curve labeled "instantaneous elongation." This is simply the stretch that takes place immediately upon application of the load and is similar to "initial stretch" or "initial elongation" used by other investigators. In this case it is largely elastic and hence recoverable by unloading. Curves labeled "1 day," "100 days," etc., include this "instantaneous elongation" and hence they show total deformation, part of which is elastic.

The graph shows the vertical endurance limit line at 6600 lb. per sq. in.[2] Thus, if the particular application involves cyclic loading, a working stress of 6600 lb. per sq. in. should not be exceeded.

Zinc and zinc alloys are influenced in their creep properties by temperature. The degree of this effect may be estimated by the following rough empirical formula derived by this laboratory from temperature studies:

$$S_T = (S_{25} \times 28) \div T$$

where S_T = permissible stress at any temperature from 25° to 100°C.,

S_{25} = permissible stress at 25°C.,

T = given temperature in deg. C.

Thus, it will be seen that for an increase of 28°C. in temperature above 25°C., the permissible stress is reduced by about half. It may be noted that zinc-alloy die castings are not suggested for uses involving continuous stress at temperatures above 100°C.

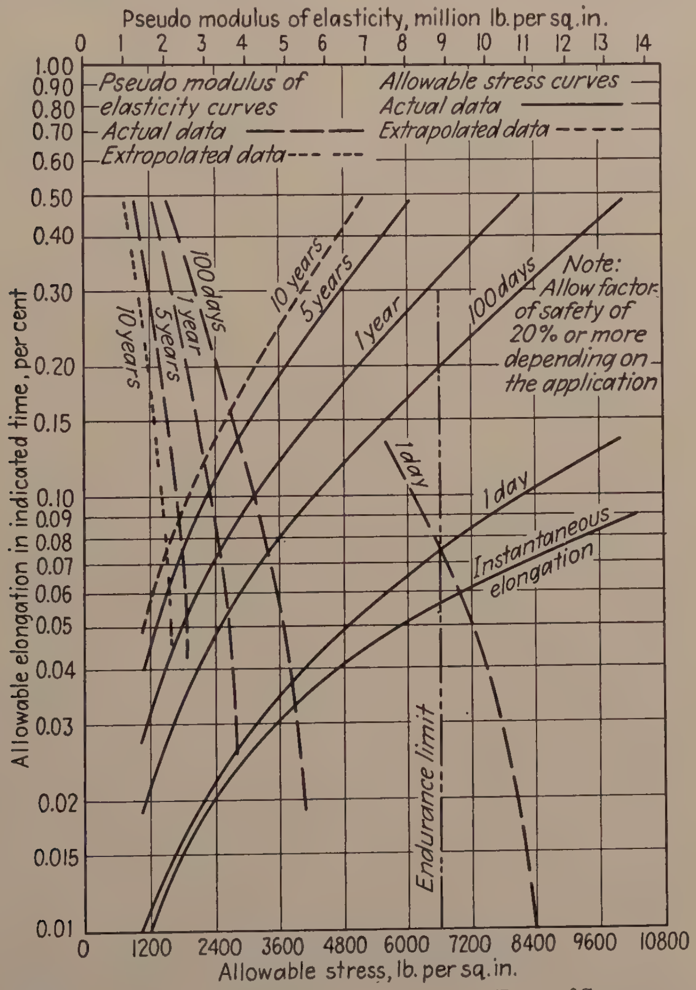

FIG. 3.—PSEUDOMODULUS OF ELASTICITY, ALLOY NO. XXIII AT 25°C. BEAM CREEP.

The charts in Figs. 2 and 3 deal only with deformation in bending. It is of interest to compare these with deformation in tension. As indicated earlier in the paper, most of the early work on creep was done by tension testing. Accordingly, there is considerable background on this point, although it was not possible to conduct so large a number of tests as was done in beam testing. A chart similar to that in Fig. 3 for beam tests is shown in Fig. 4. A comparison of the two charts will indicate that the design stresses in tension are lower than those in deflection. The reason for this probably lies in the redistribution of stresses that takes place in the bending of a beam member. By using the methods of Tapsell and Johnson, it has been calculated that the redistributed stress equals 0.74 times the initial stress. Investigation has indicated that this redistribution of stress occurs after the initial elongation, which is largely elastic. If this factor is taken into account, fair agreement is reached between tension and beam creep-test results.

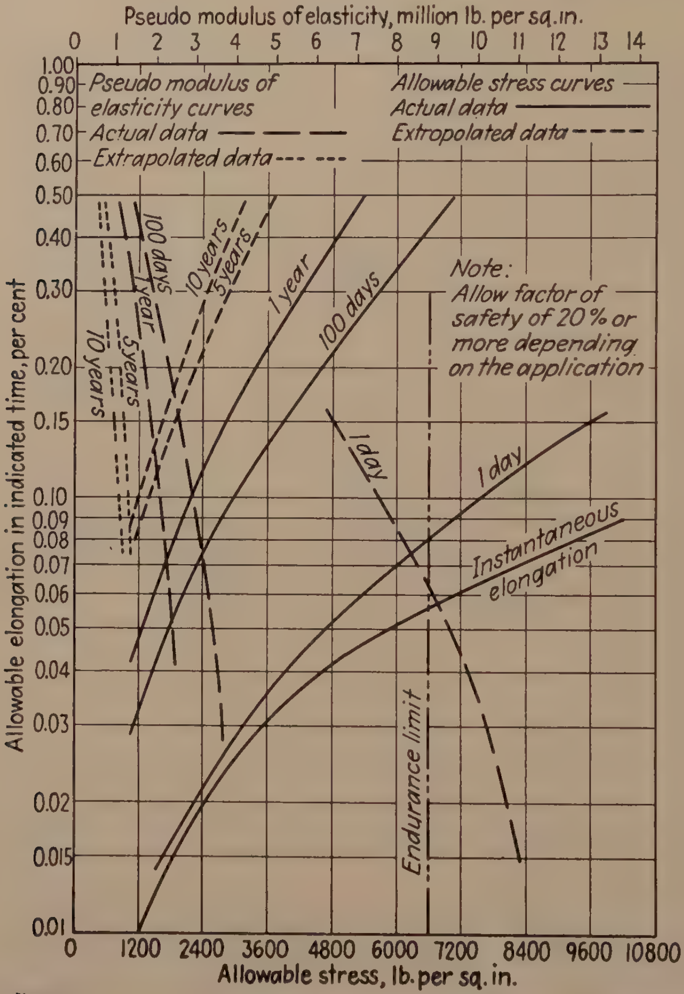

FIG. 4.—PSEUDOMODULUS OF ELASTICITY ALLOY NO. XXIII AT 25°C. TENSION CREEP.

The charts given here show data obtained on A.S.T.M. Alloy No. XXIII specimens. However, they apply equally well to A.S.T.M. Alloy No. XXV.* A.S.T.M. Alloy No. XXI* is somewhat stronger but is subject to dimensional change with aging and hence is not so desirable where maintenance of close dimensional tolerance over long periods is essential.

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* See note on page 467.

The testing work that resulted in the data presented in this paper, as well as the step by step development of technique and apparatus not described here, was not due to the efforts of any one investigator but to those of a number of investigators, hence no attempt is being made to acknowledge individual contributions.

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DISCUSSION

(*E. E. Schumacher presiding*)

E. E. Schumacher.*—Do you control the humidity in your test room? What effect does the environment have on your results?

E. H. Kelton.—We do not attempt to control the humidity. As a matter of fact, the humidity in the beam tests that were conducted in a constant-temperature room varied widely and, as far as we know, there is no effect. The tension tests were conducted largely in an oil bath. I suppose there would be an effect in highly corrosive atmospheres, sufficiently corrosive to notch the specimen; otherwise, I would say none.

E. A. Anderson.*—The effect of the humidity on the corrosion of zinc does not become important until the relative humidity is 70 per cent. At that point the corrosion products are capable of absorbing moisture and the corrosion rate increases. Below that point corrosion is almost imperceptible. This does not take into account any effect due to stress. That may be important.

E. E. Schumacher.—Recently I have become very conscious of the enormous effect that surface films can exert on the physical properties of certain alloys. Shortly, we are publishing an article in which it will be shown that the fatigue endurance of some lead alloys can be changed markedly by merely changing the type of film placed on their surfaces. Changes as great as tenfold were observed. These findings make me wonder whether in your creep test you might not obtain quite variable results, depending upon the type of liquid medium used to immerse your specimens. Did you use more than one type of oil and, if you did, what were your results?

E. H. Kelton.—I think we have used no more than three different oils, and we could not see any difference in effect.

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Creep Properties of Some Rolled Lead-antimony Alloys

By A. A. Smith, Jr.,* Member, and H. E. Howe,† Junior Member A.I.M.E.

(Cleveland Meeting, October 1944)

The creep properties of lead alloys have been studied by a number of investigators but most of the work has been done on extruded material and the amount of data available on rolled alloys is surprisingly limited. Greenwood[1] and his collaborators investigated various rolled commercial leads containing relatively small amounts of impurities, Phillips[2] likewise studied rolled commercial leads, although he did include a few alloys—such as tellurium lead and one per cent antimonial lead. But as far as the authors are aware no data on the creep properties of so-called "hard leads"—i.e., containing from 4 to 8 per cent antimony—have been published. In this paper some data are presented on a few antimonial lead alloys and compared with a copper-bearing lead.

Preparation of Specimens

All the alloys used in this investigation were cast at a temperature of 400°C. into an open cast-iron mold preheated to 100°C., the resultant casting being ¾ by 1 by 10 in. The copper-bearing alloy was cold-rolled by 10 per cent passes to a thickness of 0.100 in. Creep specimens 16 in. long were prepared by clamping the strips between wooden blocks and machining the edges of the strips parallel by means of a plane. Careful manipulation gave parallel specimens with no reduced section and with a minimum of distortion. The antimonial lead castings were hot-rolled in 10 per cent passes at a temperature of 150°C. to a thickness of 0.400 in., the heating being carried out in an electric oven after each pass through the rolls. After the castings had been broken down to 0.400 in., they were allowed to cool to room temperature and then cold-rolled to 0.100 in. with the usual 10 per cent passes. Sufficient time was allowed after each pass for the strips to cool to room temperature.

The apparatus and method of measuring strain have been adequately described in a previous paper[3] and essentially the same practice was used in obtaining the present data.

Data

Creep data were obtained on alloys of the following compositions:

Alloy	Composition, Per Cent[a]			Tensile Strength, Lb. per Sq. In.[b]
	Sb	Cu	Bi	
A	0	0.06	0.02	2,250
B	6.4	0.05	0.02	3,800
C	3.97	0.05	0.02	3,500
D	3.60	0.05	0.02	3,450
E	1.0	0.06	0.02	3,100
F	1.0	0	0.11	3,100
G	9.8	0.05	0.01	4,150

[a] Balance Pb.
[b] Tensile tests were made on the rolled strip at a straining rate of 5 per cent of original gauge length per minute.

Time-extension curves for only two alloys are given, since these are typical of all. Figs. 1 and 2 show the time-extension curves for the copper-bearing alloy *A* at 30°C. and 100°C., and Figs. 3 and 4 show

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* Superintendent of Physical Metallurgy, American Smelting and Refining Co., Barber, New Jersey.

† Research Metallurgist, American Smelting and Refining Co., Barber, New Jersey.

[1] References are at the end of the paper.

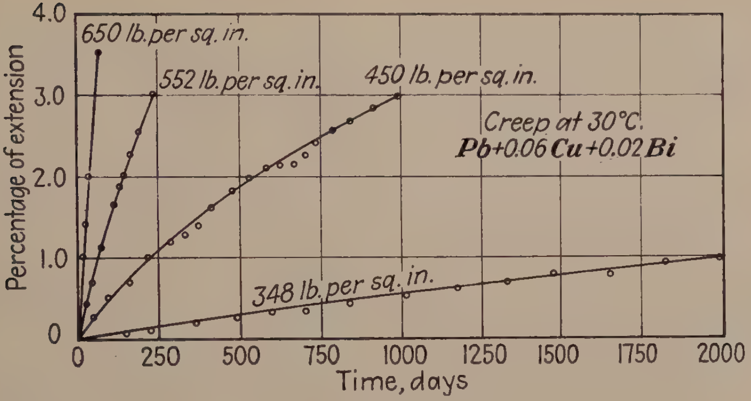

FIG. 1.—TIME-EXTENSION CURVE FOR COPPER-BEARING ALLOY A AT 30°C.

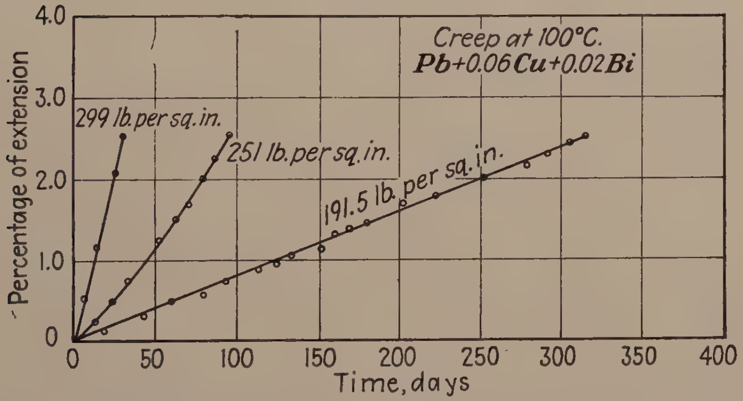

FIG. 2.—TIME-EXTENSION CURVE FOR COPPER-BEARING ALLOY A AT 100°C.

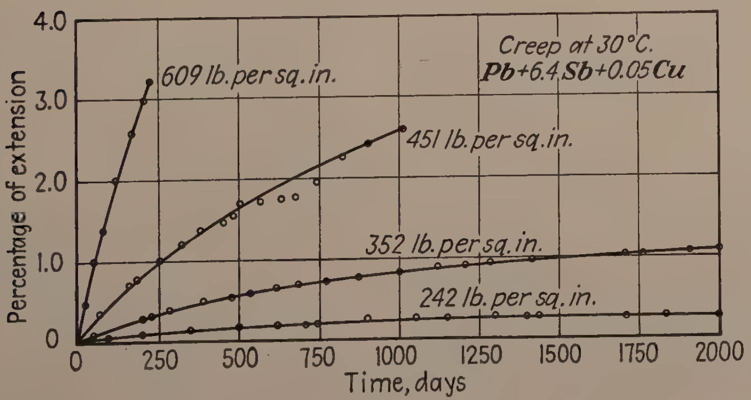

FIG. 3.—TIME-EXTENSION CURVE FOR ANTIMONIAL LEAD ALLOY B AT 30°C.

those for the 6.4 per cent antimonial lead (*B*).

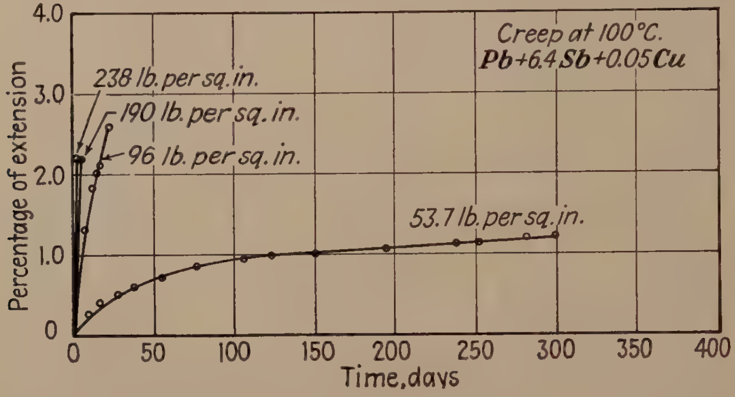

FIG. 4.—TIME-EXTENSION CURVE FOR ANTIMONIAL LEAD ALLOY B AT 100°C.

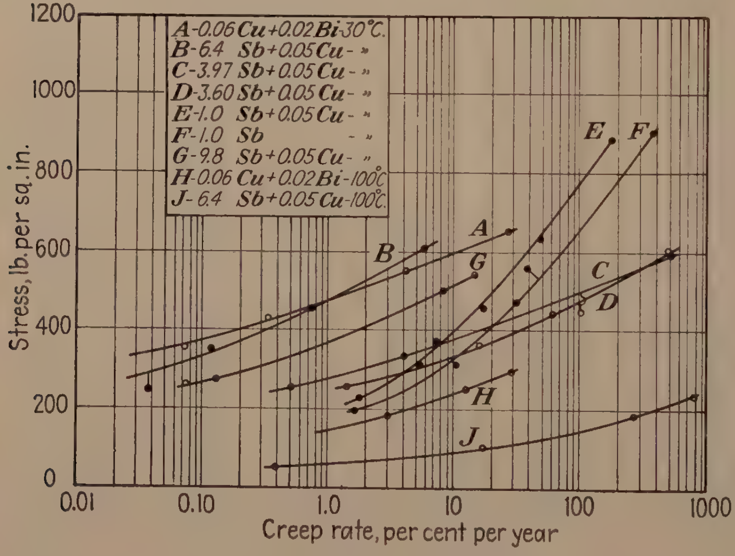

FIG. 5.—CREEP RATE OF NINE ALLOYS.

If the minimum creep rates obtainable from the time-extension curves are plotted on a stress-log rate scale as shown in Fig. 5, fairly smooth curves are obtained.

DISCUSSION OF RESULTS

Creep studies of a series of alloys is a never ending task and the data presented here are far from complete. However, certain trends are noted, which may serve as a guide to the commercial utilization of the alloys. At lower stresses the copper-bearing alloy is definitely superior to any of the antimonial leads, although the 6 per cent antimonial lead approaches it at 30°C. However, it should be pointed out that even with tests of 2000 days (48,000 hr.), minimum creep rates were not always attained at the lower stresses. Tensile strength is no criterion of the creep properties, since the copper-bearing alloy has very much lower strength than any of the antimonial alloys. Not enough data are available to definitely establish which antimonial lead alloy has the best creep properties at room temperature, although in these tests the 6.4 per cent alloy is somewhat superior and indicates that the optimum composition is probably between 6 and 9 per cent.

At 100°C. the antimonial alloy tested has very poor creep resistance—for instance, the allowable stress for a creep rate of one per cent per year is approximately 50 lb. per sq. in. as compared with 135 lb. per sq. in. for the copper-bearing lead alloy. Incomplete studies on other antimony alloys show similar trends and indicate that rolled sheet made from these alloys should not be used at elevated temperatures if appreciable stresses are involved.

One apparent anomaly is shown in Fig. 5, where the one per cent antimony alloy appears to have unduly low rates of creep at stresses above 500 lb. per sq. in. Two such alloys are given and the results on them are very similar, although those on the copper-bearing alloy is slightly better. No definite explanation of this phenomenon can be given, although it has been checked recently on another series of specimens containing one per cent antimony. One possible factor to consider is that in an alloy of this composition probably there is no primary antimony phase present in the casting, since the maximum solid solubility of antimony in lead is 2.9 per cent at the melting point and about 0.2 per cent at room temperature. Consequently, the precipitation caused by cold-rolling is entirely from a supersaturated solution, and may be of such a size or nature as to affect creep rates at intermediate stresses. All the other alloys do have primary antimony crystals present in the casting, which may act as nuclei for the precipitation of antimony during cooling and rolling, thus forming a comparatively few large aggregates. It is obvious that there must be a change in slope of the curves at higher stresses, since the tensile strength increases with increasing antimony. This supposition does not explain why the one per cent alloy is inferior at low stresses to the alloys higher in antimony, and consideration must be given to the coalescence of antimony particles in long periods of time under stress.

The data given cannot be applied to cast or extruded alloys of the same compositions, as they have very different creep properties as compared with cold-rolled specimens.

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   Greenwood: *Proc.* Aust. Inst. Min. and Met. (1935) No. 100 and (1934) No. 95.
2. A. J. Phillips: Creep Tests on Lead and Lead Alloys. *Proc.* Amer. Soc. Test. Mat. (1936) **36**, pt II, 170-193.
3. A. A. Smith, Jr.: Creep and Recrystallization of Lead. *Trans.* A.I.M.E. (1941) **143**, 165.

DISCUSSION

(*E. E. Schumacher presiding*)

E. E. SCHUMACHER.*—Mr. Smith has shown us once again how variable lead alloys can be. I have studied lead alloys for a good many years and know from experience that their behavior cannot be predicted by analogy with other alloys.

I have always been interested in observing how the creep resistance of lead may be improved by the addition of as little as 0.03 per cent Ca. Without the presence of calcium the grains of extruded lead pipe are fairly equiaxed and motion can take place easily at the boundaries. The calcium addition of 0.03 per cent causes the grain boundaries to become very irregular and jagged, and results in creep resistance many times greater than that of pure lead.

Mr. Smith showed that in the one per cent antimony-lead alloy creep is occasionally excessive even where low stresses are involved. We have observed this phenomenon many times in sleeving made of an alloy of lead and 0.7 per cent antimony, which was used for joining telephone cables maintained under gas pressure. In some instances the sleeving "ballooned" greatly in a few months; in others, where pressure conditions were presumably identical, no appreciable sleeve enlargement occurred during many service years. I cannot help but feel that many of the seemingly erratic creep results that have been reported for lead alloys would not be inexplicable if we only knew more about the effects of grain-boundary irregularities.

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* Bell Telephone Laboratories, Murray Hill, New Jersey.

E. A. ANDERSON.*—I just want to tell Dr. Smith that he is not alone in his tribulations about finding an explanation for the curve of that alloy with one per cent antimony. The matter of different types of alloys having different slopes in regard to their log-creep rates at different stress levels was encountered by us in connection with a zinc-titanium alloy that we reported on last February.

What we have found is that a so-called solid solution type of zinc alloy, such as one per cent copper, will have a lower creep rate at high stress than an alloy of this zinc-titanium type in which the solid solubility is low.

However, at low stress the two curves have crossed and the copper alloy has a much higher creep rate than the zinc-titanium alloy.

We are still searching for an explanation, but I think we and Dr. Smith are dealing with the same general type of thing, in that the zinc-titanium alloy we suspect has a dispersion precipitation effect.

MEMBER.—I wonder whether the speaker has done anything to determine the effect of the storage time afterward.

A. A. SMITH, JR.—When it comes to storage time on age-hardening lead alloys, many different factors come into play. We have tested a number of them, but frankly we have not all the answers. On these rolled alloys, the rolling apparently causes complete precipitation, because we have had samples aged for long periods of time and then tested in creep and there seems to be very little difference in them. But that is not true of cast alloys of antimony or extruded alloys of antimony, because in these two cases the casting is supersaturated with respect to antimony and precipitation takes place at room temperature, and very marked changes take place. In fact, on extruded lead alloys, we have almost given up as a hopeless job the correlation of the data we have. There seem to be so many factors involved in the aging that it is difficult to control all of them.

Here is a very curious one. We have a one per cent antimonial lead that was heat-treated; that is, it was heated to near its melting point, quenched and aged for a year, and then it was hung in creep. We had six or eight different loads on the samples from that particular alloy and in a period of a few weeks the first sample broke with no detectable elongation. A few weeks or months went by and another sample broke under a lower stress, with no measurable elongation during the testing time. That has continued now for 11 years. Out of the eight samples, there are still two on test, six having broken over a period of time from a few weeks up to six or seven years and none of these samples showed any elongation whatsoever.

We have taken the same alloy, at least the same composition, and repeated the tests, and in this case we do get elongation. So I do not know how to correlate all the factors on these age-hardening alloys, particularly where changes are taking place at room temperature or at the testing temperature. The factors are so involved and so complicated that a great deal of work will be necessary to correlate the data and understand what is taking place.

E. E. SCHUMACHER.—Several years ago we were extruding some lead-1 per cent antimony alloy on a small experimental press. We had taken great pains to have all extrusion conditions identical with those encountered on larger presses used in one of our manufacturing plants. When the extruded product was tested for various physical properties, it was found that the tensile strength was about 400 lb. per sq. in. lower than that found on factory extruded material. Since the extrusion rates, pressures, cooling cycles, etc., were all identical, we were quite baffled for several weeks. The only difference, which at one time seemed unimportant to us, was that in the factory the hot cable was reeled and the corresponding strip in the laboratory was not. We then investigated the effect of hot-working through reeling immediately after extrusion. By use of reeling procedures in the laboratory, devised to simulate those in the factory, we were able to duplicate the tensile strengths of actual cable-sheath material. This experience indicates how easily the properties of lead alloys may be changed.

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* New Jersey Zinc Co., Palmerton, Pennsylvania.

In working with lead alloys, we should also always remember that at room temperature they are much closer to their melting points than are most other alloys. I am confident that a great deal would be added to our knowledge by studies of these alloys at temperatures considerably below room temperature.

A. J. Smith, Jr.*—There seems to be a good deal we do not know about what is happening above the recrystallization temperature of any of these materials when we start studying them under stress. Entirely apart from this lead story, about 12 years ago I was heat-treating a 4.5 per cent high-purity aluminum-copper alloy, rather coarse grained, in a ½-in. test bar. The grains were perhaps 5 or 6 mm. in diameter. I inadvertently dropped the bar on the floor and it broke in the middle of the gauge length. It had the most beautiful fracture you would ever want to see. Every grain was just like a mirror. The two ends of that bar have been handled by everyone who has come through the laboratory and one thing people always like to do when they see a nice shiny surface is to handle it. You know from the microsamples when a salesman comes through. So when people saw the fractured end of the bar, on went their fingers. The remainder of the bar, which was machined, has become discolored and corroded. In spite of the salt on the people's hands, the fractured end, which was handled so much, is just as bright today as it was 12 years ago. What is taking place at that grain boundary?

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* Lunkenheimer Company, Cincinnati, Ohio.

Symposium on Continuous Casting

(New York Meeting, February 1944)

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The Joint Session on Continuous Casting, of the Institute of Metals Division and the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers, convened in the Jade Room of the Hotel Waldorf-Astoria, New York City, on Feb. 23, 1944, at 9:15 o'clock, Carl E. Swartz presiding.

C. E. SWARTZ.—It is gratifying to see so many out at what may seem an early hour for the beginning of A.I.M.E. sessions, but I think this number—some fifty or sixty of you—is an adequate expression of the interest in these processes all over the United States, and possibly in foreign countries.

I would like to ask those who feel that this type of program is of value to you to write or speak to some one of the Institute of Metals Division officers and suggest other topics for symposiums. We have a feeling that some of these current practices are of interest and we believe that under proper sponsorship many of the companies will be willing to give publicity to processes such as those that will be discussed today. Also, we would like suggestions and criticisms, so that the next ones can be better.

The subject of continuous casting is not new, of course. The two papers on the program this morning will adequately cover the history and some of the earlier processes, some of the theory and some of the practice, some of the reasons why these various methods did not work. I was rather interested in discovering, when thumbing through one of the A.I.M.E. publications the other night, an article on continuous casting. I was not aware that the A.I.M.E. had published any papers on continuous casting, but there may be a number. The one that I happened to find was published in the 1915 volume, on the Mellen rod-casting process, and so we might say this is not the first session in which these subjects have been under discussion. However, there have been many improvements since then in all fields of metallurgical and mechanical engineering; consequently, I think that the papers today will be a little more involved and a little more complete in their technique.

The first paper today will be given by one of our gentlemen of the press, who has done one of the outstanding jobs in this country in calling to our attention some of the newer processes that are being considered and being used in the metallurgical indus-

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try. Several years ago he had a series of two or three articles in *Iron Age*, which were excellent writing for the metallurgist and engineer unfamiliar with the process. If medals were available for such an activity, Mr. Lippert should have received a medal, because those articles on continuous casting are excellent even today.

So I am sure there is no one that can open this symposium more fittingly than Mr. T. W. Lippert, Managing Editor of *Iron Age*. Mr. Lippert.

Continuous Casting Yesterday and Today

BY T. W. LIPPERT,* MEMBER A.I.M.E.

IN these opening remarks, I will endeavor to give a background of continuous casting of metals. Only passing attention will be given to the different processes to be described by the authors whose papers are on the program, as they are far more familiar than I am with their subject matter.

Suffice to say that over the past several years the brass, copper, aluminum and magnesium industries have shifted practically completely from conventional static molds to continuous casting machines. The Aluminum Company of America alone has more than 60 continuous machines in operation.

The product as continuously cast is superior metallurgically, less scrap loss is involved, costs are generally lower, and the equipment requires little floor space. A continuous machine, operating as it does with deadly constancy, is a ravenous consumer of molten metal, and in most plants one or two machines are well able to handle large banks of melting and refining furnaces.

In steel, interest in continuous casting is today more serious than ever before in history, and there is every reason to believe that continuous machines may secure a minor place in the ferrous industry, particularly for tool and alloy analyses. In the past, steel has been commercially cast continuously, and today many tons of steel are being turned out in this manner.

It has been said that the cradle of every science is surrounded by dead theorists—and certainly there are innumerable examples of this in the metals industries. An excellent illustration, for instance, is the continuous rolling of metal, a tantalizing objective that for decades on end exhausted the efforts of a long line of famous, infamous and unknown inventors. Finally, in 1922, John B. Tytus, of the American Rolling Mill Co., brought forth what now seems such an obviously simple scheme—a concave roll face, each stand of progressively less concavity. And out of this one change in design sprang today's wide continuous mill rolling steel sheet 100 in. wide at 2000 ft. per minute.

Another excellent example is the continuous casting of liquid metal into an intermediate form, preferably one requiring little subsequent breakdown.

First, the casting of liquid metal alone was fascinating enough. Then someone passed the cast metal directly into a rolling mill, and shortly thereafter this continuously rolled strip was passed directly into a stamping machine. This *leitmotiv* of a continuous flow of metal from the liquid phase to a consumer end product, fast and inexpensive, and all housed within a small space, was enough to drive some 200 or so inventors into frenzy over the past hundred years. All the ideas, however, like mayflies, had only their brief afternoon of existence. They were born and they died on paper, as constant exemplification of that great void that always exists between mental production and commercial production.

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* Editor, *The Iron Age*, New York, N. Y.

History of Process

Credit for starting the ball rolling is conventionally given to the famous Englishman, Sir Henry Bessemer, who early in 1858 suggested that the then successful rolling of glass plate between two rolls from the liquid phase could perhaps be adapted to a similar rolling of soft metals. Some 10 years later he actually gave it a try, successfully rolling a 40-in. length of wrought-iron strip, said to have excellent surface and metallurgical properties. But Bessemer's idea (American Patent No. 49053) came long after a method of continuously casting soft metal tubing, wherein the mandrel was vibrated to prevent sticking, was conceived by J. Laing, in 1843 (American Patent No. 3023). With nationalism in temporary eclipse, the proper crediting of the original ideas may not be of much importance at this late date, but, since today's commercial continuous casting processes resemble Laing's far more than they do Bessemer's, perhaps some of the accolade for being the father of continuous casting could be shifted from the shoulders of England's illustrious Bessemer to that of America's unknown Laing.

Following Bessemer and Laing, the next important twitch in the technology of continuous casting came during the period 1890 to 1900. In 1891, E. Norton and J. Hodgson successfully rolled some steel sheet by pouring liquid metal between two rolls. The results were promising, but work was abandoned because of lack of money and time. At about this same period the Washburn and Moen Manufacturing Co., of Worcester, became greatly interested in continuous casting of round billets. Washburn, Daniels and Stover, of that company, set down a number of excellent observatons on such casting through a vertical, open water-cooled mold.

A little later J. O. E. Trotz, of the same company, elaborated these ideas and is accredited with establishing some lasting principles of continuous ingot casting. But, no machine actually was ever built. Trotz became superintendent of the South Works of American Steel and Wire Co. (which had absorbed Washburn and Moen), and after some years retired to Sweden and died there some seven or eight years ago.

Also, during this same period (1890), B. Atha (from which, Atha Works of Crucible Steel Co.) devised a long, vertical open mold, with a single water jacket, for continuously casting 4 by 4-in. steel billets. This equipment was in constant operation up to the year 1910, and it is believed that some thousands of tons of liquid steel was processed in this manner. Only high-carbon file steel was cast continuously at Atha, and while there are reports that the billet surface was none too satisfactory, the metal generally fulfilled all commercial demands. The arrangement was to set a crucible of metal on top of the mold and withdraw the billet by means of pinch rolls.

By 1900, practically every conceivable idea on continuous casting had been pawed over and set forth in patents by a long line of known and unknown inventors. There were infinite variations of casting the molten metal between metal rolls, with exquisite nuances of mold design, cooling technique and auxiliary equipment. The same applied to pouring between chains of half molds carried on continuous belts, or of pressing, sucking and pouring of molten metal through all kinds of vertical, horizontal and slanted mold arrangements.

The next definite effort to actually physically cast metal came in about 1914. At that time, J. T. Rowley successfully cast some lengths of steel through a vertical mold at the U. S. Horse Shoe Co., Erie, Pa. But a young man, fresh from college, by the name of Grenville Mellen, blew a surge of new life into the idea of casting between mold halves carried on two continuous belts, first suggested in detail back in 1885 by A. Matthes and H. W. Lash. Remarkably little is known of the Mellen efforts, considering the fact that the work did not fold up until about 1925. During the period 1914 to 1925, considerable financial support was given Mellen by Spencer Watters, of the New York Cotton Exchange. Probably Mellen is still living, but it is not known where.

Mellen went to the general machine shop of Thompson, Coates and McKay, of Harrison, N. J., early in 1913, to have a small horizontal chain machine built for casting solder. Attention was later shifted primarily to brass, and about 1914 the machine was transferred to the Standard Underground Cable Co., Perth Amboy, N. J. During this interval the idea of a horizontal machine was discarded in favor of a much larger vertical chain machine. In 1915, Mellen had his patents assigned to the Continuous Casting Corporation, and the machines were all shifted to Gar Wood, N. J., where they became the seed from which grew the Gar Wood Brass Corporation, a war enterprise of considerable size, which completely disappeared from the industrial scene by 1925.

Mellen was a clever theorist and devised many improvements in the chain casting technique and metal-feeding techniques. He also was quite an amateur athlete, and for years did a great deal of wrestling around eastern New Jersey as the "Masked Wonder," the mask being worn to conceal his identity. He usually won the matches, too.

The Mellen vertical chain casting machine had individual mold blocks (or half blocks) of cast iron, about 5½ in. long and 5 in. wide. The machine was 12 ft. in height over all, 2 by 3 ft. in horizontal cross section, and 6000 lb. in weight. It had a framework of cast iron, holding in position the two endless chains of mold blocks, which were made in sections and joined by pins in center alignment.

Casting speed was about 25 ft. per min. for ⅞-in. brass rod, and mold-block temperature was about 450°F. even with some water cooling. In all, about 1000 tons or so of commercial brass rod, mostly 1½-in. rounds of cartridge brass, was cast in this machine. No trouble was experienced with the molds, but the greatest difficulty was experienced in getting the proper flow of molten brass to the point where the mold halves came together. The tip of the silica tube used to transfer the molten brass from the crucible to the pouring point had a tendency to burn off; or the metal would back up and partially freeze, and yank off the entire tube. Elaborate methods of minimizing this tendency were devised, but the accurate control of metal flow was the basic difficulty, and in the end was greatly responsible for abandonment of the process. The Gar Wood Brass Co. subsequently ceased to exist and the machine was scrapped.

There is to this day some interest in the idea of casting molten metal continuously by means of numerous half molds linked together in two continuous belts, wherein the molds come together to form a casting chamber, and stay together long enough so that the resultant billet can support itself, then separate so that the belts can carry the mold halves back to the casting point. The practice seems simple and foolproof.

In 1930, J. Chantraine, a Frenchman, with some fanfare prophesied great things for such a method, which he had devised. He spoke confidently of quality of product and economy of operation, and came up with the curious method of cooling the molds with refrigerated air rather than water, but there is no evidence that such a machine was built. Today, the Dortmund-Hoerder Huettenverein, in Germany, is supposed to be using a vertical machine of this type, but with what metal and how successfully is not known. Also, it is believed that Dow Chemical Co. once experimented with a vertical chain machine for magnesium alloys, but if so the idea was abandoned, for this company now employs a conventional open vertical mold for large extrusion rounds.

The next definite period of continuous casting activity came around 1940. In the strip-sheet field, C. W. Hazelett had a number of wide casting-rolling mills in experimental operation; and Merle was doing some work with high-speed film casting of strip. The continuous casting of rods and ingots was showing great promise. A number of Alcoa direct casting machines were in operation, Poland and Eldred were successfully producing quality copper rod, Williams was experimentally casting steel billets, and Junghans had one billet-casting machine in operation on brass in this country.

But today the picture has again shifted and expanded. Work on continuous cast sheet or strip has faltered or died, and many of the machines are scrapped. As regards continuously cast ingots and bars, however, the technology has expanded dramatically. In fact, one process not described here has, during the past year or so, continuously cast some thousands of tons of commercial steel billets.

Summary of Processes

A brief outline of interim changes and current status of continuous casting may be given as follows:

Hazelett Process

The inventor, himself, has to some extent lost interest in the continuous casting-rolling of wide strip sheet. Hazelett's activities today are rather of a political nature, attempting to interest Washington policy makers in his idea of "incentive taxation" as a means of encouraging industrial enterprise. For this reason the utilization of Hazelett mills has sagged drastically. The units of the International Nickel Co. (20 in. wide) and the Scovill Manufacturing Co. (12 in. wide) have both been scrapped. The Crucible Steel Company's 15-in. mill is still at the Atha works, but inactive. The Aluminum Company of America's 30-in. mill, probably the best ever built by Hazelett, was sold to the Harrison Radiator Division of General Motors Corporation, Lockport, N. Y., and a great deal of experimental work is being done on the rolling of copper and brass. Results to date have been very encouraging. The Crown Cork and Seal Company's 24-in. mill has been sold to the Winchester Arms plant at New Haven, Conn., which has an exclusive Hazelett license for rolling zinc, and currently is inactive. This accounts for the five domestic mills. Of the three units sold in Japan, nothing is known of the 32-in. mill for zinc, which was sold to Mitsui Mining Co., or of the 20-in. copper and brass mill sold to Furukawa Advices prior to Pearl Harbor indicated, however, that the 16-in. brass mill in the Sumutomo plant was in operation.

The Harrison Radiator work at Lockport has suffered considerably because of the war, but despite difficulties of roll deterioration and end-dam cracking the company is diligently pursuing the problem and believes that results to date promise a successful future for the Hazelett machine. A great deal of excellent brass has been rolled on this unit for the Army, in 6-ton heats, the continuous strip being up to 30-in. wide. The mill is now working on copper, and probably will handle the copper strip requirements of the plant after the war.

J. M. Merle Process

The Merle high-speed process for film-casting a thin steel strip onto a moving steel belt, or onto a cooled wheel rim, is apparently inactive. The three or four machines built for the Allegheny-Ludlum Steel Corporation have all been scrapped. The inventor, now in Chicago, is said to be interested in developing a continuous "cast-drawn" pipe machine for a Brazilian steel company.

Junghans-Rossi Process

Six Junghans-Rossi units are in commercial operation on brass and light metals—one unit in England and an unknown number in Germany. Well over 500,000 tons of metal has been cast in this equipment.*

Poland-Eldred Process

The American Smelting and Refining Co. and the Chase Brass and Copper Co. together have purchased all Eldred patents to combine with their own patent structure on the continuous casting of copper rods. One very successful machine is in operation at Perth Amboy, N. J., and new units are likely to be built.

Both the Eldred and A. S. and R. (Poland) machines specify the use of graphite molds with no lubrication, and because of the use of thick graphite molds the heat transfer is very slow. Thus, the casting rate is very slow, being on the order of 6 or 8 in. per min. maximum. A curious characteristic of the Eldred and the Poland patents is that they specified diametrically opposite modes of thermal transfer from the molten metal to the coolant. Whereas Eldred particularly specified withdrawing the heat down through the congealing metal, Poland equally specifically specified withdrawing the heat through the mold walls and not through the congealing metal. In any case the difference in opinion is of little moment now.

Because of Eldred's longitudinal heat withdrawal, the crystal orientation of the metal was longitudinal, and because of the slow heat withdrawal the crystal sizes were sometimes enormous. In one instance a copper rod was produced as a single crystal some 32 ft. in length. All this favored the production of metal that was gas-free and very dense, and frequently with exceptional mechanical properties. And, often the metal surface may be so perfect as to make unnecessary a scalping operation prior to subsequent hot or cold working.

A. S. and R.'s machine is essentially a refractory (graphite) chamber holding a sizable quantity of molten metal, with automatic temperature recording auxiliaries for holding the metal within close limits and with facilities to protect the metal against oxidation. In the bottom of this chamber are set four graphite dies along with their individual cooling arrangements. The continuously cast rods are individually withdrawn from these dies and either reeled or cut into lengths by saws. The machine works continuously, day and night, and if after several hundred hours of service a particular graphite die should wear it can be removed and a new one replaced without interrupting the casting in the other dies. The multiple die arrangement of course overcomes the disadvantage of the very slow production of a small cross-sectional cast of metal from each die, and the unit as a whole has a most respectable output, on the order of several thousand tons monthly.

The machine is not in the least temperamental in operation. Naturally, there are innumerable fine points of die design, and inter-relationship between cooling location and speed, and casting speed which have by trial and error been built up into a volume of plant "know how," all of which is a major factor in successful operation of the equipment.

Alcoa DC Process

The Alcoa DC Process is a highly successful ingot-casting method, with more than 60 units in operation in Aluminum Company of America plants, and licensed units in operation in the plants of Extruded Metals, Tube Turns, Bohn Aluminum and Revere Copper and Brass, Inc. This machine will not be described today, and for that reason perhaps a little more information on this unit may be of interest.

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* See page 495, this symposium, and *Iron Age* of Feb. 24, 1944.—EDITOR.

The mold sizes vary from 8 in. to 16 in. in diameter for round extrusion ingots; sheet ingots vary in cross section from 6 × 22 in. to 12 × 48 in.; and squares for blooming mill work vary from 8 × 8 in. to 18 × 20 in. in cross section. Some of the older units cast in 90 in. lengths, whereas the newer units cast in lengths in the neighborhood of 140 in. These sizes apply for both aluminum and magnesium, although magnesium sheet ingot cross sections are usually of the smaller size mentioned. In magnesium emphasis on round castings for extrusion is expanding considerably with the growing tendency to pre-extrude all strip billets, a practice for years common with I. G. Farbenindustrie in Germany.

A particular DC machine casting 11-in. round billets in the 17S analysis, in lengths approximately 10 ft. long has an output of about 25,000 lb. of metal every 8-hr. turn, but this output can vary considerably depending on ingot size, number of molds being poured simultaneously, and analysis of metal being poured.

In the case of the machine mentioned, the 17S alloy has a furnace temperature of 1375° to 1385° F., and passes down a runner to a cast-iron distributer pan, equipped with four cast iron nozzles, individually controllable, each of which feeds a casting chamber. Metal temperature in the pan is, say, 1270° to 1325° F., and a metal head of about 5 in. is maintained in the pan.

The molds are simple aluminum (53S) tube sections 10 in. in length, set into a steel plate framework. On occasion 2S alloy is used to make the molds, and this analysis stands up to heat erosion better but will not take the bumps and tears of 52S. Copper and brass molds likewise have been used, but here again mold performance, particularly as regards tearing, does not equal the 52S aluminum analysis. About 25 per cent of the solidification of the aluminum takes place in the mold. The bulk of the heat, however, is extracted from the metal by means of water sprays located at the mold exits.

A hydraulic platform underneath the molds drops down at a speed of about 3 in. per min. carrying the four casts with it. The entire cast (or drop) takes about 40 or 50 min. at which time the ingots are some 10 ft. or more in length, depending on the size of the particular furnace heat. At the end of the cast, the distributer pan is removed, the platform is lifted sufficiently to loop crane slings around the ingots and lift them from the pit. Subsequently the platform is again lifted to floor level, the distributer pan again set in place, and everything readied for another cast. Of course, if so desired, the platform arrangement could be replaced by pinch rolls and automatic cut-off saws in much the same manner as the Junghans (Rossi) arrangement.

E. R. Williams Process

Work on a unit for continuously casting steel billets by the Williams process has been shifted to the Republic Steel Corporation, Cleveland. Results so far are indefinite.

Mr. Williams undoubtedly will deal at length with the work now underway, using the equipment he has devised over the past years at his plant at Latrobe.

It is frequently held that the continuous casting of steel is pretty well limited by mold deterioration, and by slow speed because of the great quantities of heat that need be withdrawn.

For these reasons it might be of interest to note that on several trial runs the steel was poured at near the freezing temperature of 2600° F., and the mold coolant rose about 15° in temperature when circulating at 150 gal. per min. At this rate the water was picking up about 18,000 B.t.u. in about 6 sq. ft. of mold surface. And, since in the very best of high duty boiler installations of modern Naval design the maximum heat exchange is on the order of

3000 B.t.u. per sq. ft. per min., the opinion was that at the 8 ft. per min. speed the casting of the 3 × 8½ in. section was progressing just about as fast as theoretically possible in order to freeze the entire cross section to a solid.

In actual practice, however, only the outer skin of the ingot need be frozen in the mold, the interior being solidified as the result of water spraying below the mold. For the 3 × 8½-in. section, a total of, say 10 sq. in. of outer cross section would be fully sufficient to solidify in the mold. This would permit a *theoretical* casting speed far above the 8 ft. per min. used in the experiment cited above.

Parenthetically, it might be pointed out that when the Bethlehem Steel Co. experimented with continuous casting of steel in 1941, somewhat similar conclusions were reached. The Bethlehem setup was comparatively simple. A copper mold was water-cooled by means of five sets of copper coils fastened to the outside surface of the mold. Bethlehem cast 4-in. rounds, and made about 30 casts in all. Speeds of 15 ft. per min. were reached, but optimum speed seemed to be 8 to 10 ft. per min. Carbon steels, from 0.1 C to 0.5 C were tried, and thermal cracks were found in all analyses above 0.3 C. In general, the surface condition was poor, with laps, folds and bleeding. The mold itself seemed to stand up well and the coolant showed no large rise in temperature. A secondary cooling spray was located around the bottom of the mold. The experiment, however, was abandoned because of pressure of other work, and not very many definite conclusions were established.

But, all the mold refinements being worked out by Republic, together with some alterations in the handling of coolant to additionally improve the scouring of heat off the interior of the mold wall, may possibly open the way to faster speeds and serve to stabilize the operation considerably, the result being that a year from now this unit can well be of great interest to the entire steel industry. For, like all continuous casting operations it may be a means whereby a relatively small capital expenditure can furnish immediate break-downs for rod and wire mills, and perhaps be a means of locating some small plants in remote areas to handle local requirements and to draw upon surrounding scrap supplies.

N. P. Goss Process

N. P. Goss has developed a method of continuously casting steel billets with a sectional mold having constant internal lubrication. Results so far are indefinite.

U. S. Steel Corporation Process

In addition to the interest one U. S. Steel Corporation subsidiary has in the Goss process, the Corporation also has patented a somewhat unique continuous casting machine, and intends to give it an experimental whirl. The significant feature of the machine is the casting (or extrusion) of a ceramic mold around the liquid metal as it is cast into a billet. This mold is broken away after the billet cools, and is re-used in part or discarded. Such a mold is being used in an effort to avoid as far as possible the severe heat withdrawal imposed by a short metallic mold. The method may be employed for various carbon tool steels.

R. K. Hopkins Process

Originally the R. K. Hopkins process was used for continuously casting alloy steel onto the side of a carbon-steel ingot, at the plant of Allegheny-Ludlum Steel Corporation. This method is a unique procedure, which can be considered a continuous casting possibility. What makes this practice so very unique is that molten metal is not brought to the machine from a conventional refining unit, but rather is produced right in the mold by what is essentially a precision electric arc furnace, continuously fed with exact predetermined quantities of raw materials which melt to form an alloy steel under a carefully controlled refining and protective slag. A moderate-sized machine can easily melt, refine and cast even the most complex of alloys at a rate of over one ton per hour, and this pace can be stepped up considerably without much difficulty.

Dow Process

One 12-in. Dow machine is in operation and two 18-in. machines are being built, for casting Dowmetal extrusion rounds. The unit has a single, open, vertical mold chamber. The cast ingot does not drop down to a hydraulic platform, as in the Alcoa DC process; rather, it is pulled down by pinch rolls and cut to extrusion lengths with a flying saw, as in the Rossi process. The Dow casting speed is midway between the Alcoa and the Rossi speeds.

Reynolds Metals Process

One unit of the Reynolds process is in operation on aluminum-alloy ingots. It has a definite physical resemblance to the Alcoa DC machine, but the mode of operation may be different.

Inco Process

The Inco process utilizes a bar and billet-casting machine devised by the International Nickel Company of Canada. It is used at the American Metals Company's plant at Carteret, N. J. Inco of Canada has one unit in operation on copper at Copper Cliff, Ontario.

The Carteret machine continuously casts 3-in. square copper wirebars or 3-in. piercing billets at a rate of about 4000 lb. per hour. The copper is continuously fed from one of two melting furnaces, through a closed runner, to the mold chamber. The mold is copper, with many internal passages for coolant. Particularly interesting is that the mold is split in two parts axially, and these parts vibrate very rapidly to overcome friction; the amplitude of the vibration being very small, or less than enough to break the surface tension of the molten metal entering the top. Metallurgical characteristics of the metal are excellent and surface condition of the bar is so good that scalping is not required prior to manufacturing operations. This machine is very successful in all respects, and additional installations are to be expected.

Soro Process

The Soro process certainly cannot be said to fall neatly within the generic boundaries of continuous casting—in fact, it is not continuous casting; it is centrifugal casting with some specialized technical ramifications. Nonetheless, the end objective of all continuous casting schemes—that of using a small, comparatively simple and inexpensive piece of equipment to congeal molten metal into either a finished product or a precise and quality product a couple of jumps beyond the semifinished stage—is fulfilled by the Soro process. And because of this once-removed kinship, the Swiss method can justifiably be fitted within the pattern of continuous casting, and weighed and judged by the same technical and economic considerations applied to the more obviously conventiona methods.

The Chairman.—The second paper this morning is going to cover history also. However, Mr. Goss is going to use a little different method of attack in that he will emphasize the metallurgical theory a little more than did Mr. Lippert. Mr. Norman Goss.

The Continuous Casting of Molten Metals—History, Requirements, Metallurgy and Economics

By N. P. Goss,* Member A.I.M.E.

What would appear to be a very simple process on paper has proved to be overrun with a multitude of unseen difficulties. For more than 70 years attempts have been made to cast metals in a continuous manner, but it has been only within the last 10 years that some degree of success has been achieved.[1]

Historical Development

Bessemer's Experiments—Method 1

Bessemer was the first to try to cast molten metal in a continuous manner. His method is fully described in U. S. Patent No. 49053, issued in 1865. The patent drawing is shown in Fig. 1. In this method the molten metal was poured between a pair of rolls of large diameter, which were cooled by water sprays. Means were provided to prevent moisture from coming into direct contact with the molten metal.

The width of the strip was controlled by the flanges. On paper this should work to perfection, but it is beset with many difficulties still awaiting solution. Bessemer failed to reduce his invention to commercial practice.

About 1890 Bessemer's method was revived by Norton and associates (U. S. Patent No. 441375). They formed the Fluid Metal Rolling Co. at Maywood, Ill., and spent $250,000 in endeavoring to develop the technique for this simple method. Finally they had to abandon it. Naturally, they did carry the technical development far beyond anything Bessemer had done, but even so it was far from being a useful commercial success.

In recent years it has undergone further development by C. W. Hazelett (U. S. Patent No. 2058447), who has succeeded in obtaining long lengths of copper, brass, aluminum, and even stainless steel. He introduced many ingenious devices but the greatest obstacle still remained—the disintegration of the roll surface when the surface is heated and chilled in rapid succession. Difficulty is also experienced in maintaining a uniform supply of molten metal to the rolls. The patents pertaining to this method would indicate these to be the major obstacles.

Experimental Work by Mellen—Method 2

A departure from the method introduced by Bessemer was tried by Grenville Mellen, of East Orange, N. J., sometime between 1914 and 1920, who obtained a number of patents.[2] His method is illustrated in Fig. 2. This method failed to make an impression upon the art; however, it is of value in pointing out the difficulties the inventor ran into and the way in which he tried to meet them.

The split mold sections form two endless chains. When going through the center of the apparatus, these sections engage each other to form a complete mold. As the engaged mold section moves downward at a constant speed, molten metal is teemed into it. As this is going on, another set of cooperating mold sections move into position on top of the one being filled. The molten metal is teemed into the mold through a silica tube. According to the teachings of this patent, the level of molten

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Manuscript received at the office of the Institute March 10, 1944.

* Consulting Engineer, S. Euclid, Ohio.

[1] References are at the end of the paper.

metal must remain fixed, automatically controlled, and splashing absolutely prevented.

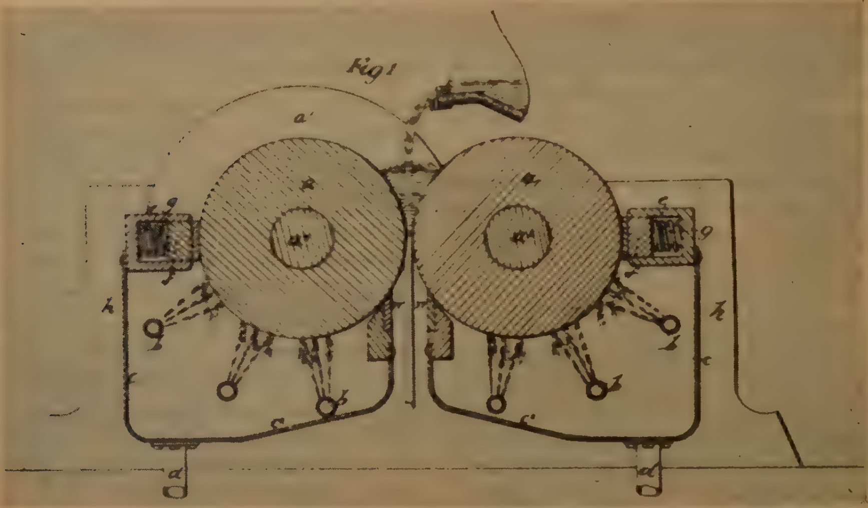

FIG. 1.—BESSEMER PLAN, FROM PATENT 49053.
The reference numbers in all reproductions of patent drawings shown in this paper refer to the descriptions in the patent records. No explanation will be found here.

When the mold sections are engaged, all joints must be airtight. To accomplish this a most elaborate mechanism was required.

Mellen apparently experienced considerable difficulty with sticking. How he overcame this is described in U. S. Pat. 1321658. Herein the importance of thoroughly cleaning the chill surfaces is emphasized. The cleaning and applying of grease was done automatically.

While apparently he succeeded in mastering these and other mechanical difficulties, the one remained—the gradual distortion of the mold sections. This was caused by the rapid heating and cooling each section undergoes. When this distortion became excessive, the mold sections could not be properly engaged, and molten metal would find its way into the voids thus formed, which made it difficult to operate the machine.

Even if this machine could be operated, its construction is so elaborate that it would be entirely too costly to operate.

There are a number of patents on machines similar to Mellen's (for instance, A. Matthes and H. W. Lash, U. S. Patent 342920) but all have failed to make any impression upon the art. It is doubtful whether any of them were ever tried experimentally.

The lesson to be learned from the experiments of Bessemer, Norton, Hazelett, and Mellen is the difficulty of using moving chill surfaces. No one has yet found a material that can withstand heating and chilling in rapid succession without undergoing deterioration.

The Stationary Mold—Method 3

A radical departure from the Bessemer and Mellen machines seems to have been introduced by Tasker in 1879 (Patent No. 223077). This method is illustrated in Fig. 3. The inventor of this machine attempted to cast steel tubes by pouring molten metal into one end of a stationary water-cooled mold provided with a mandrel, and extracting the solidified metal from the other end. This method must have been new to the art in that the application was filed Oct. 6, 1879, and issued Dec. 30, 1879. From the description given in the specification, one suspects that he actually tried to cast tubes, but it is also quite logical to conclude that it did not work. Anyone who has tried to cast metals in molds of this type can point out a number of reasons why this design failed.

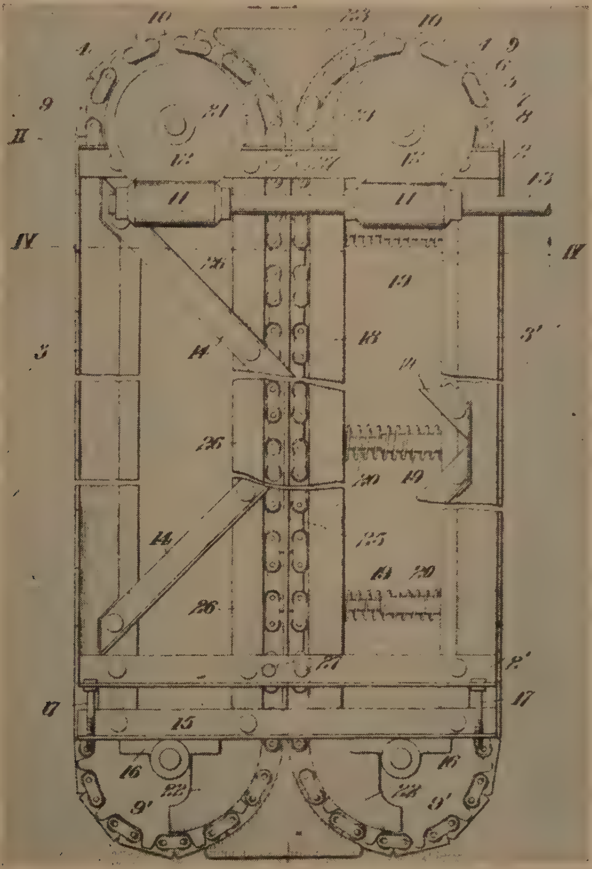

FIG. 2.—MELLEN PATENT 1321658.

About 1890 a patent was issued to B. Atha (U. S. Patent 425486), which described a method of casting ingots in a stationary mold. Whether Atha actually tried to cast ingots in this way is not known to the writer; however, from the detailed description given in the specification of his patent, one may infer that he did try it. The mold was water-cooled and resembled a big-end-down ingot mold. The ladle containing the metal was attached directly to the mold. Means were provided to heat this feeder ladle. To begin the operation, a dummy bar was inserted into the mold and brought to the top. The downward movement of the dummy bar and the filling of the feeder ladle was carried out at the same instant. A feature of this method was that the ingot was not withdrawn from the mold in a continuous manner, but intermittently. This was done to permit sufficient solidification before the ingot was permitted to come out of the mold. Like Mellen, Atha stressed the importance of not allowing the molten metal to surge or stream upon the mold walls as this caused grooving and scouring of the walls. He claimed that by bringing the dummy bar clear to the top of the mold before teeming, disintegration of the mold walls was prevented.

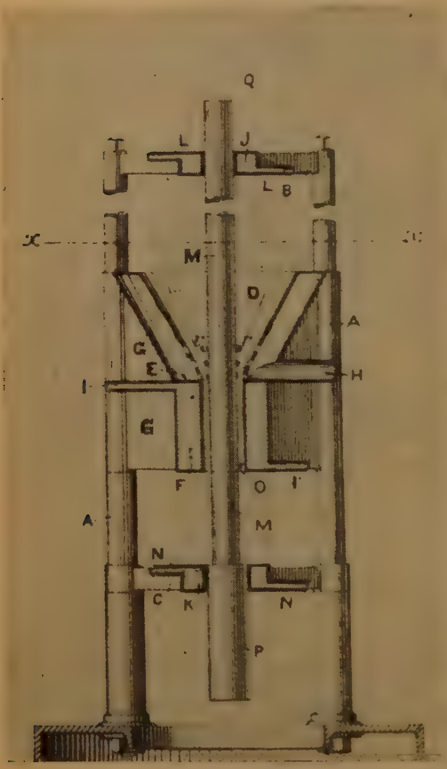

FIG. 3.—TASKER PATENT 223077.

Atha's objective was to eliminate the formation of "pipe" and improve structure generally. In general, this has been the objective of all who are trying to develop continuous casting.

Around 1900, Trotz, a contemporary of Norton,[1] greatly improved the structure of the stationary mold. There are in all about five Trotz patents, and while it is said that he never tried his method experimentally, he set forth many of the major difficulties that must be solved in order to make the method function in a practical manner. In one patent he describes how buckling of the mold wall was prevented (Patent No. 705721). Fig. 4 shows the patent drawing. This construction permits longitudinal expansion of the mold. The upper end is more or less rigid, but the mold tube is loosely fitted at the bottom end of the mold so that it is free to move in the longitudinal direction. The joint between the mold tube and water jacket is made nearly water tight. If desired the tube could be mounted in the water jacket so that longitudinal expansion could take place freely at both ends. Trotz also stressed the

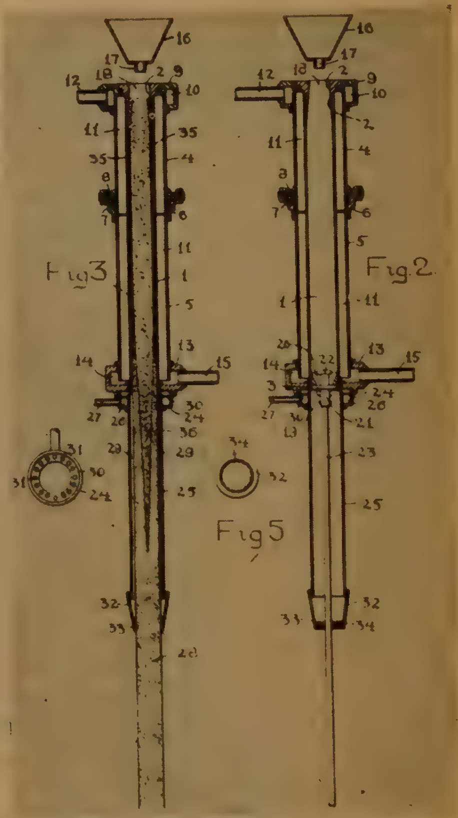

FIG. 4.—TROTZ PATENT 705721.

importance of having the mold walls perfectly straight and polished. The provision to compensate for longitudinal expansion and the polishing of the mold walls were believed essential for the free movement of the ingot, as otherwise it would stick or hang in the tube.

The metal was fed into the mold by means of a nozzle extending down into the mold and molten metal. This prevented spattering, which, if permitted, would cause the molten metal to adhere to the mold walls. This also fed the metal into the mold without turbulence and thus prevented formation of blowholes and pipes.

It should be noted that Trotz did not use any lubricant to reduce the frictional movement of the ingot in the tube; at least, it was never mentioned in his patents.

In Patent No. 894410, issued to Trotz in 1908, an addition to the original mold is described. This was called a tempering chamber, which according to the specification, was to perform a number of useful functions; i.e.: (1) to reduce the friction upon the moving ingot; (2) to provide a means of further supporting the easily deformed ingot from bulging; (3) to permit the temperature of the surface and interior to become equalized; (4) to prevent excessive oxidation of the surface of the ingot.

The tempering chamber was slightly larger than the mold, and the supporting of the ingot surface was supplied by steam under considerable pressure. This tempering chamber was not water-cooled; however, the steam going through the space provided was to prevent excessive heating of the tempering chamber.

Whether the tempering chamber functioned as described is not known. Apparently Trotz was unsuccessful in that his method failed to make any impression upon the industry, which is the yardstick by which one measures failures and successes.

It would seem that the measures he took to prevent sticking, buckling and frictional resistance were not the answer to the problem.

The Monnot Patent

The Monnot patent, No. 944370, was issued to John F. Monnot and assigned to the Monnot Metallurgical Corporation, New York. Whether any experimental work was carried out is not of record. The patent specification would lead one to believe that some work was conducted but whether the results obtained, if any, had anything new to offer is not known.

The apparatus proposed is shown in Fig. 5. The molten metal was teemed through a layer of fused wiping material, such as borax or glass, and after going through the flux flowed into a continuous casting mold, similar to the one proposed by Atha. The mold was made of short sections, bolted together, and had a slight taper, to facilitate the movement of the ingot through the mold.

The method was developed with the idea of producing a flawless ingot and, in particular, to prevent piping, entrainment of the occluded gases and remove inclusions, etc., that contributed to inferior quality; and with the idea that hot metal does not always remove the internal defects introduced during casting of the molten metal in the ingot mold; and that a considerable part of the ingot had to be scrapped because of the inferior quality of these portions.

Experimental Work of Rowley

About 1920, Rowley attempted to cast forging bars in a stationary mold of the type shown in Fig. 6, reproduced from his French patent No. 479927. A machine similar to the one presented here was built by the Arthur McKee Co. and set up for operation at the U. S. Horseshoe Co. of Erie, Pa.

The split mold was 8 ft. long, provided with a slight taper, and was yieldably joined by means of springs. This would permit the mold to give slightly if the casting, sliding through the mold should tend to engage the chill surface with excessive friction. The mold was mounted in a suitable framework to allow for the longitudinal extension that must occur when the inner surface of the mold becomes heated. Obviously, if the dimensional changes the mold must undergo when the casting moves through are not taken into account, the chill surface might become warped to the extent that the billet would hang in the mold.

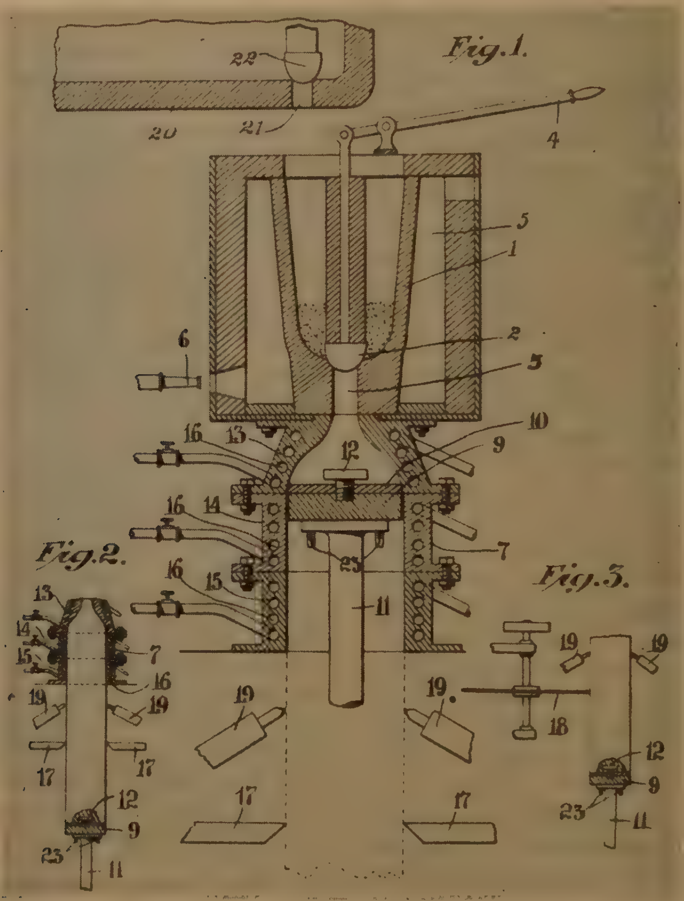

Fig. 5.—Monnot Patent 944370.

Rowley cast square billets ranging from about 1¾ to 3 inches.

The ladle was attached directly to the mold. The mold was made of cast steel and the chill surface was much thicker than in the mold used by Trotz. The pinch rolls were mounted directly below the exit end.

In one of the trials, Rowley succeeded in obtaining a bar 150 ft. long. The runout table was too short to handle a billet of this great length, so everyone in the shop grabbed a pair of tongs and carried the bar through the plant and out into a field full of weeds. Because of the crude manner in which this bar had to be handled, it looked like a giant cobble. The surface was rough, and bulged, and the bar was necked down in many places.

During the casting operation, it was observed that the bar was necking down between the pinch rolls and the exit end of the mold. Suddenly the bar would pull loose and go through the pinch rolls at its normal rate of speed. This slowing down of the rate of extraction occurred a number of times. The necking down was probably due to the bar sticking in the mold, but the pinch rolls exerted a sufficient pull to sever the adhesions. The adhesion of the surface of the billet to the mold wall may have been responsible for many of the surface defects.

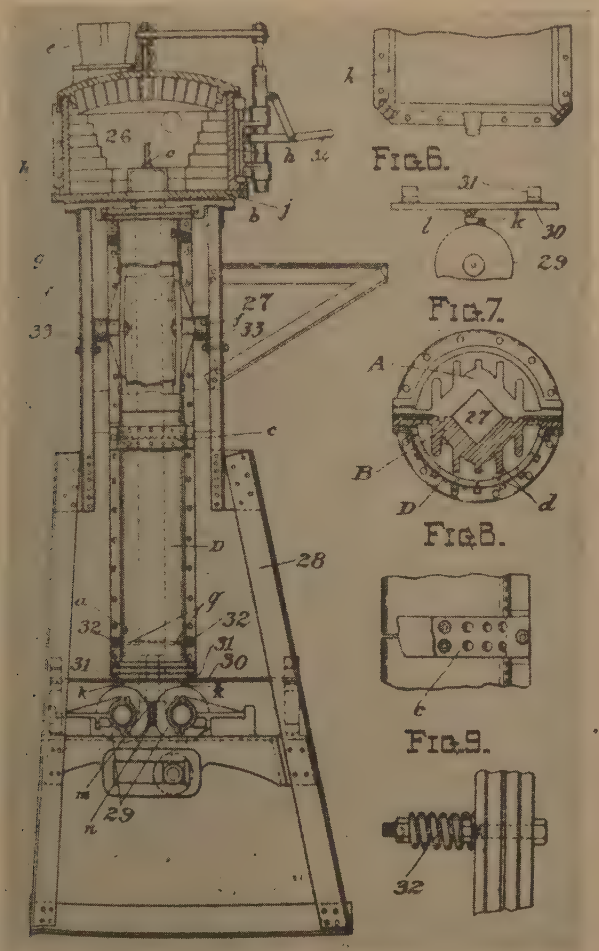

Fig. 6.—Rowley, French Patent 479927.

While this was the longest bar cast, a large number ranging from 20 to 40 ft. in length were also obtained. It seems that the greatest difficulty was experienced from the metal freezing in the nozzle and sticking in the mold.

The chill surfaces were examined from time to time and were found to be fairly smooth, except at points where adhesions had occurred. The chill surfaces did not appear to be warped; apparently the mold was rugged enough and mounted properly to resist distortion.

Incidentally, the 150-ft. bar was cut into forging bars and worked into horseshoes of good quality.

The pioneer work of Rowley was interrupted, unfortunately, when the U. S. Horseshoe Co. failed. While Rowley was granted numerous foreign patents, none were obtained in the United States.

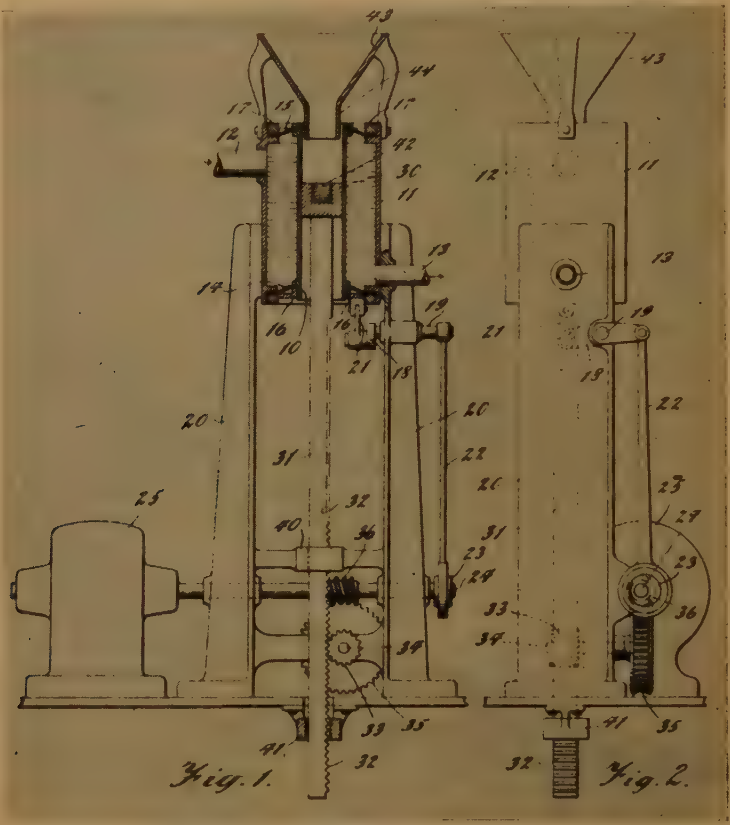

Fig. 7.—Van Ranst Patent 1385595.

The Van Ranst Patent

A reproduction of the patent drawing of the Van Ranst structure (Patent 1385595, in 1921) is shown in Fig. 7. The water jacket is stationary. However, the molding tube, 10, is caused to vibrate by mechanism, 21. The constant longitudinal vibration of the mold prevents the metal from freezing to the mold as it solidifies. The inventor pointed out that the novel feature of his method was the relative movement of the mold and the metal being cast, so that adherence between the two is prevented; and that the relative movement may be derived in various ways—for example, when casting circular bars, the mold may be rotated or oscillated.

The Pehrson Patent

Pehrson was one of the first to suggest the use of a reciprocating movement of the mold relative to the casting to prevent the metal sticking to the wall of the mold. His patent was No. 1088171.

However, neither the Van Ranst nor the Pehrson machine appears to have had any influence upon the art. It remained apparently for Junghans to work out a successful procedure for this method, but it must be pointed out also that Junghans lubricated the mold with oil from time to time. The question, then, is, how essential is the lubrication to the success of the reciprocating type of mold?

The Junghans Method

Junghans has developed a continuous casting machine (German Patent No. 510361 in 1930), which is operating successfully on brass. Whether this machine is capable of casting steel is a matter of speculation. A Junghans machine was reported by Lippert[1] to be in operation at the Scovill Manufacturing Co. at Waterbury, Connecticut.

The feature of the Junghans method is that the mold and billet move down at the same rate for a distance of about 1¾ in. and then the mold snaps back quickly to its original position, the snapback speed being about three times the speed of the billet. The purpose of this snapback is to prevent sticking and rupture of the skin. From time to time oil is sprayed on top of the molten brass, some of which is carried down between the ingot and the mold wall. This, no doubt, reduces the frictional movement of the ingot through the mold and minimizes sticking. Apparently Junghans has found one way that permits the casting of nonferrous metals in a continuous manner and on a commercial basis.

W. T. Ennor Patent

The W. T. Ennor method of casting aluminum (Patent No. 2301027) was developed to meet a demand for structurally sound aluminum and magnesium ingots of large cross section and of indefinite lengths for forging and structural shapes. According to this patent, it is virtually impossible to cast these metals in the conventional ingot molds when the cross-sectional area exceeds a certain size. Such ingots were not sound and were difficult to shape into finished articles without cracking. Also, the structure lacked uniformity and the response of the finished article to heat-treatment was extremely erratic. These undesirable characteristics demanded a new technique in the casting of aluminum and magnesium.

Ennor found that the size and distribution of the alloying constituents governed the working characteristics. When the segregations were present in the form of large bodies scattered at random through the ingots, it was difficult to work the ingot mechanically.

However, when the various constituents were more uniformly distributed throughout the ingot, it was much easier to deform by mechanical working. Furthermore, the quality and response to heat-treatment was much more uniform. Cracking was found to be due entirely to large bodies of segregated material, and no amount of hot-working could effectively destroy this undesirable structure.

Some improvement was obtained in the conventional mold, when the metal was made to solidify gradually from the bottom to the top. While this produced an ingot suitable for many requirements, it failed to solve the problem of segregation.

The ingot having the properties desired was obtained only when the metal was cast in a continuous manner.

In the Ennor method, the heat is initially removed from the molten metal without metal-to-mold contact. The principle of the method is illustrated in Fig. 8. The metal is teemed into a trough to which a feeding device is attached to maintain a constant level of molten metal in the mold. This arrangement also provides a means of introducing the metal without turbulence. The importance of this has been cited in several of the patents already described; for example, Trotz Patent No. 705721.

The mold is cooled by spraying water directly on it. The inner walls of the mold are coated with a layer of grease, wax, or similar substance, to prevent the molten metal from contacting the mold wall. The molten metal is cast into the mold against the layer of lubricant, which remains on the mold walls even after an ingot of considerable length has been cast.

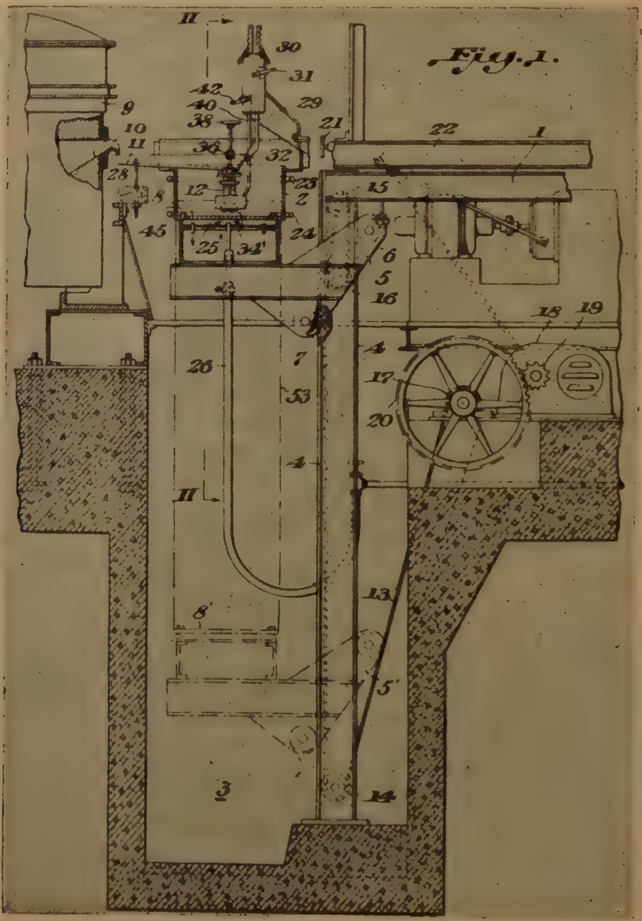

Fig. 8.—Ennor Patent 2301027.

The metal is extruded from the mold at 1 to 7 in. per minute. The mold is very short in that the distance from the exit end of the mold to the top of the ingot is only 4 in. The metal is continually teemed into the parabolic-shaped pool of metal filling the top of the ingot. The ingot leaves the mold when the solid skin of metal is strong enough to support the molten interior. The rate of casting is governed largely by this condition. Obviously, if the casting rate is too great, bleeding or bulging occurs, and this is minimized by water-cooling the ingot as it leaves the mold.

The Eldred Patent

Eldred was perhaps the first to develop a successful continuous casting machine (Patent No. 2048734). The type he devised is shown in Fig. 9. Instead of a mold made of copper, one of graphite is employed. Graphite has an extremely high thermal conductivity, is nonwetting, refractory, and self-lubricating and therefore meets all the essentials of a mold material for many nonferrous metals. Eldred has been interested mainly in producing copper rods of greatly improved structure, and it must be said that his method achieved the result he sought to attain. The improved metallurgical structure is obtained by controlling the direction of solidification, which is along the length of the casting, little heat being removed through the mold walls. This is the feature of this method and, while producing excellent metal, it is very slow.

Poland and Lindner

Many of the more recent patents on continuous casting of nonferrous metals seem to favor the use of a graphite mold. While all of these patents may appear the same, they differ greatly in detail. Very often some slight modification, which may not appear of much importance to the layman, greatly improves the process of continuous casting.

Without question, these slight improvements will eventually increase the speed of casting and further improve the product.

Poland and Lindner, like Eldred, prefer to use a graphite mold (Patent No. 2136394). They point out that this material must not only be refractory but that it must have, in addition, an extremely smooth finish and be of extreme density. (It will be recalled that Trotz, in one of his patents issued around 1900, stressed the importance of a smooth finish.) A feature of their invention is the use of a graphite having a definite particle size, so that maximum extreme density of the graphite is realized. The die wall was tapered slightly to facilitate withdrawal of the congealed metal.

With the introduction of this extremely dense die material, having the characteristics described, copper and copper-base alloys could now be cast continuously by extracting the heat through the walls of the mold. When billets 3 in. or more in diameter are cast, mold taper may be dispensed with as the contraction of the copper on solidification is sufficient to provide adequate clearance.

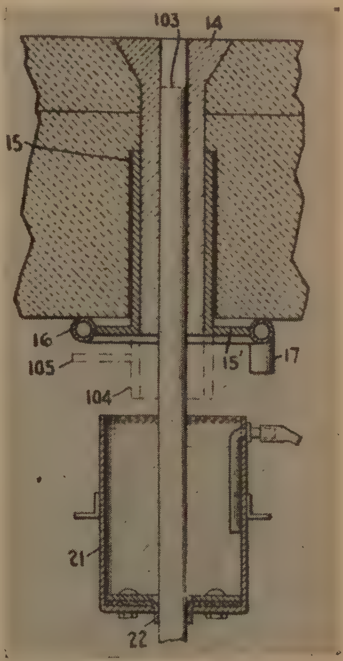

FIG. 9.—ELDRED PATENT 2048734.

In the Eldred process the heat is largely removed by conducting it down the already congealed copper, which is an excellent heat-conducting material.

The Eldred, Poland and Lindner patents differ entirely in the manner in which the heat is removed and in the requirements of the die material.

Patents have been issued to Betterton and Poland for improvements; Patent No. 2291204 deals with a slip-preventing means and Patent 2195809 provides a means of avoiding turbulence and deep head in the mold. When a deep head of metal was used, the copper undergoing solidification in the mold had a tendency to come out of the mold with a checked surface and at times even to break in two.

ranging from 4-in. squares to 4 by 8½-in. slabs. The mold structure is shown in Fig. 10 (Patent No. 2079644).

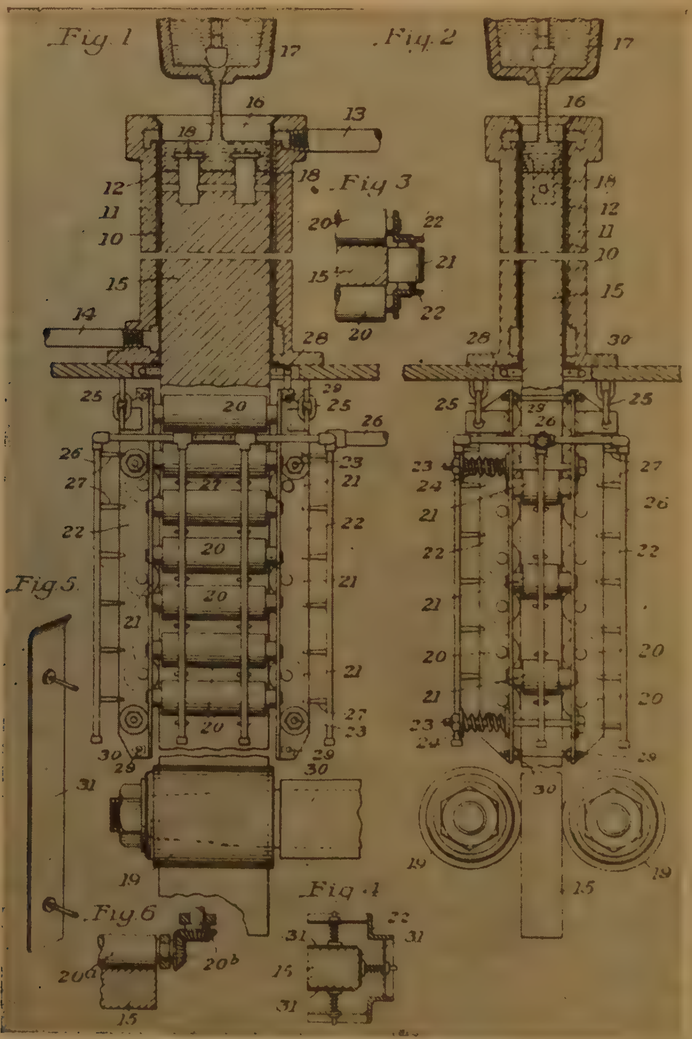

FIG. 10.—WILLIAMS PATENT 2284503.

The Williams Patent

Williams has been experimenting at Latrobe, Pa., on casting of both ferrous and nonferrous metals although during the past several years his work has been almost entirely on steel. He has successfully cast plain carbon, alloy, and stainless steels in a large variety of shapes and sizes,

The mold has a thin wall of high thermal conductivity and a thin sheet of water moving with high speed over this mold wall.

The purpose is to remove the heat as rapidly as possible and to form a skin on the ingot, which will shrink away from the frictional resistance of the mold wall and have sufficient strength to prevent rupture as it moves along the mold wall.

When the heat is dissipated with extreme rapidity from the outer surface of the mold wall, a high-temperature gradient is then established. The greater the temperature gradient between the ingot surface and the mold wall, the faster will the heat be removed from the inside of the ingot.

Williams did some additional experimental work at the Battelle Memorial Institute, and found that where the chill surface of the mold was lubricated greater casting speeds would be possible; as described in Greenidge Patent No. 2206888.

In this method casting speeds as high as 12 ft. per minute have been obtained.

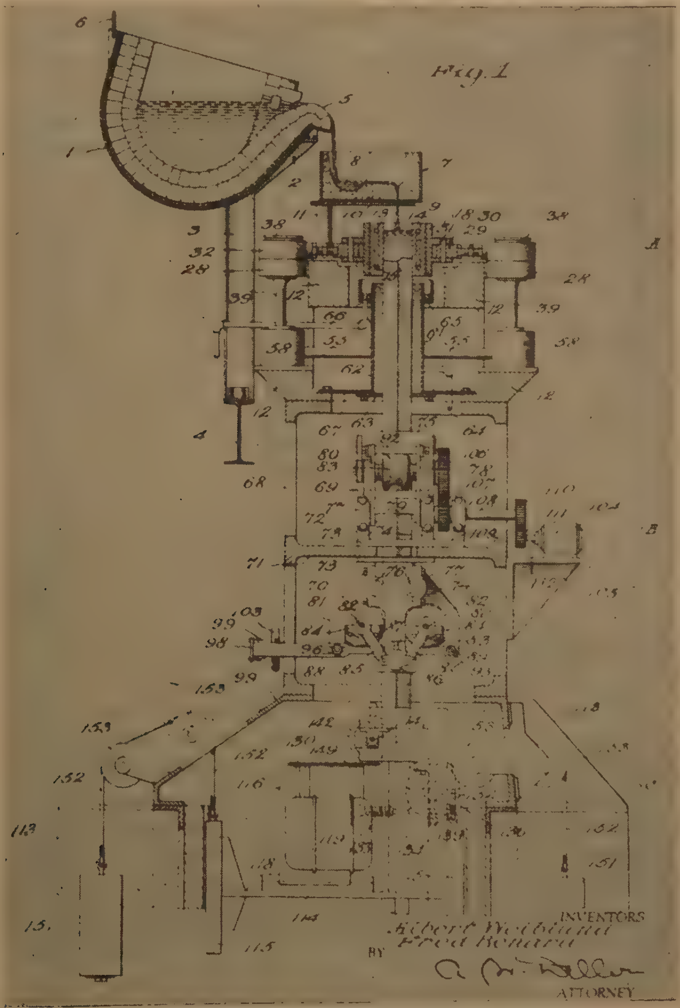

Fig. 11.—Welblund and Benard Patent 2284704.

Articles by the inventor and Lippert[1] have described the process in greater detail.

Welblund and Benard Patent

The type of machine developed by Welblund and Benard (Patent No. 2284704) is shown in Fig. 11. It is a modified stationary mold, consisting of two split water-cooled sections, which are vibrated at a definite and controllable frequency during the casting operation. The method is set into operation in the same way as the conventional stationary mold.

The specification points out that many attempts have been made to cast metals and alloys in a continuous manner, but many were not successful. The efforts of the early workers failed to develop an apparatus capable of overcoming the inherent difficulties, one of which was sticking or adherence of the solidified metal to the mold wall. When this happens, it is virtually impossible to pull the casting through the mold without damaging the surface. Such castings are commercially unacceptable and the process could not be operated very long after pieces of the skin froze to the chill surface of the mold.

The inventors found that sticking of the metal congealing in the die could be prevented by using a split die, the sections being given a slight but rapid vibration perpendicular to the axis of the mold. The mechanical vibration of the mold does not have a deleterious, but rather a beneficial, effect on both the surface and inner structure of the casting.

In one experiment, a mold 9 in. long, capable of casting a 3 by 3-in. copper ingot, was used. It was cast at about 10 in. per minute, and a casting 70 ft. long was produced. The mold was vibrated somewhere between 100 and 1500 times per minute, and the amplitude of the vibration varied from 0.002 to 0.050 in. The inventors point out that the mold sections need not touch each other in the position of minimum clearance. They mate with each other closely so that there is substantially no clearance between them in the closed position, although preferably they do not touch. Even with this small air gap, varying from 0.002 to 0.05 in. continuously, ingots produced were free of fins. The patent drawing shows that the mold sections are short and of rugged construction and, therefore, should resist distortion quite well. It is obvious that if the mold sections would warp unduly, successful operation would be impossible.

The copper cast by this method was found to be free of fissures, cold shuts, etc. Likewise, the ingots are free of pipes, shrinkage, cavities, and other defects. Welblund and Benard presented a mass of physical and metallurgical data to support their claims.

REQUIREMENTS OF CONTINUOUS CASTING

The patent literature clearly shows that the success of continuous casting depends largely upon the construction of the mold and the manner in which the metal is teemed and extracted from the mold. While the basic or fundamental principles of continuous casting are well understood, much remains to be done before the method will be ready for commercial exploitation on a large scale.

Of the various methods proposed, the stationary mold as introduced by Tasker, Atha, and Trotz appears to be the most logical one to use. The patent literature of recent date seems to bear this out.

The layman may not appreciate why so many patents should be granted on a method disclosed more than 50 years ago, and why so many of them appear so similar. It must always be kept in mind that while the basic principles of the method have been known for many years, very few have been able to overcome all the difficulties that arise when metals are cast continuously. Therefore, each patent covers certain details that may in one way or another overcome the inherent difficulties and bring the method closer and closer to success. On reading the specifications of some of these patents, one may even miss the improvement introduced unless one is familiar with all the details of the method.

Certain problems are inherent in the forming of continuous ingots, slabs, billets, etc., direct from the molten metal. The cast piece must be formed within the confines of the ingot mold. Molten metal is teemed into one end of the mold and the solidified piece removed from the other end, either continuously or intermittently. Heat transfer is indirect; first the heat is absorbed by the chill plate and through to the water. Most metals shrink or contract when cooled. This results in a drawing away of the metal from the walls of the mold, leaving an air gap across which the heat transfer is greatly retarded. Difficulty is also experienced by the metal sticking to the mold surface, distortion of the mold, great variations in the frictional resistance of the casting moving through the mold, and turbulence of the metal being teemed into the mold. These are the problems that must be solved in order to make the method workable. Trotz recognized many of these difficulties, but the methods he devised failed to meet the requirements. The object then is to find practical expedients to overcome these obstacles.

The mold or continuous casting device must have the following characteristics:

1. It must have good thermal conductivity.
2. It must resist distortion.
3. It must resist disintegration when subjected to the intense heat of the casting moving through the mold.
4. The chill surface must be nonwetting and smooth, to facilitate movement of the casting through the mold.
5. The mold must not rupture when water-cooled.
6. Metal must be teemed into the mold with a minimum of turbulence.

So far two materials have met these requirements, copper and graphite. The thermal conductivity of copper is extremely high, and the thermal conductivity of dense graphite is excellent and closely approaches that of aluminum.

Copper molds are preferred, not only for their excellent thermal conductivity but also for their excellent resistance to fracture when molten metal comes in contact with the water-cooled surface. Another advantage of copper is that the thermal conductivity[3] does not drop appreciably over considerable temperature changes; i.e., up to 1200°F.

Distortion of the mold is largely a matter of design. Trotz directed much of his experimental effort to solve this vexing problem. Apparently, the expedients he devised failed to prevent distortion. While it may not be possible to prevent distortion entirely, it certainly can be reduced to an insignificant figure.

It is quite obvious that once the chill surface becomes distorted or warped, the movement of the casting becomes difficult, because of the increased frictional resistance between the mold wall and the surface of the metal sliding through. When the frictional engagement between the surface of the casting and the chill surface becomes sufficiently large, two things may happen:

1. The surface may be ruptured at local areas, permitting bleeding.
2. The ingot may hang in the mold and be pulled apart.

The problem of buckling or warping of the mold or chill surface has continually frustrated the efforts of many inventors.

In the stationary mold, distortion can be controlled, as exemplified by the Junghans and the Eldred machines, for casting nonferrous metals such as copper and brass. However, in continuous casting devices like the Mellen machine, in which a number of moving parts are used, warping can never be overcome until a material is found that will resist distortion when the mold sections are subjected to rapid cycles of heating and cooling.

The main difficulty with the bessemer method is the disintegration of the chill surface due to fire checking, also caused by the rapid cyclic heating and cooling of the chill surface.

The problem of mold distortion and disintegration of the chill surface becomes more difficult to master the higher the melting point of the metal cast.

The chill surface must be absolutely nonwetting and smooth. Graphite meets this requirement and for this reason is extensively used as a mold element for casting nonferrous metals continuously. A nonwetting surface prevents adhesion and sticking of the metal passing through the mold. Should the metal going through the mold stick to the chill surface at localized areas, the free passage of the casting becomes difficult because of the increased resistance to the free passage of the metal through the die at such points. When the adhesion is severed, some of the metal may stick permanently to the surface of the mold and continue to build up until the passage is so restricted that the casting will hang in the mold and be pulled apart by the tension exerted by the pinch rolls, if they are powerful enough to do so.

It would seem that the early inventors did not appreciate the importance of a nonwetting surface, although many of the recent patents stress its importance.

Mechanism of Solidification

When molten metal first touches the mold, a fragile skin of solid metal forms. The thickness and the temperature of the skin thus formed depends upon the heat-absorbing capacity of the mold. The skin, immediately upon forming, tends to shrink away from the mold wall, forming an air gap between the casting and the chill surface. The magnitude of the air gap thus formed depends to a large degree upon the hydrostatic pressure the molten interior exerts upon the fragile solidified skin. If the hydrostatic pressure is small, the air gap will be large; if the hydrostatic pressure is strong, the air gap may be small.

When the solidified surface shrinks away and leaves a large air gap, it becomes reheated and weakened to the extent that rupture occurs and the molten interior issues through the fracture formed. Upon coming in contact with the chill surface, this metal freezes and forms undesirable wrinkles and these may scour the surface of the mold and even adhere to it.

The problem then is to control the air gap and the magnitude of the frictional resistance of the casting passing through the mold.

As the solidification process proceeds, the surface of the casting is continually making and breaking contact with the chill surface at many points. In other words, the mold wall and the surface of the casting are never in intimate contact at all points at the same time, therefore it is important to prevent the frictional contact at these points of localized contact from becoming excessive. If this is not taken into consideration, the surface of the casting will stick to the mold wall or even fracture.

Therefore, as the casting moves through the mold the hydrostatic head is continually increasing and the thickness of the solid shell enclosing the liquid interior is also increasing. The air gap and the frictional resistance with which the surface contacts the mold at localized points is dependent therefore, upon the magnitude of the hydrostatic pressure exerted upon the skin of solidified metal.

When the solidified shell is able to support the partially solid interior, the casting no longer requires the support of the mold but after it has left the mold the cooling is usually continued, to prevent the interior from overheating the surface.

So one is confronted with the problem of preventing the formation of a large air gap and excessive sliding friction.

In general, a copper chill surface is not nonwetting, and suitable materials must be applied to it. However, they must not impair the thermal heat transfer. Greenidge

(Patent No. 2206888) and Ennor (Patent No. 2301027) applied grease to the mold wall before casting, while Junghans[1] and Pehrson (Patent No. 1088171) applied it during the casting operation.

According to the Greenidge patent, the coating or film of grease may function as follows: It behaves as a thermal conductor to continue the heat transfer between the ingot and the mold, and it is quite likely that without some sort of material supplied to the air gap there never would be good thermal contact between the two. In its passage through the mold the casting is continually contacting and shrinking away from the chill surface at many points. Consequently, some sort of self-accommodating material is essential to fill the air gaps that form and at the same time prevent too much sliding friction from developing between the ingot and the surface of the mold. Besides maintaining good thermal contact, the self-accommodating material should also be capable of reducing the frictional resistance to the movement of the casting in the mold. Greenidge Patent No. 2206888 suggests that, by reducing the frictional resistance, a thinner skin on the ingot will resist rupture.

The molten metal must be introduced into the mold with a minimum of turbulence. When the metal is teemed into the mold without agitation, the fragile skin, which forms the instant the metal touches the chill surface, will be free of cold shuts, folds, and many other undesirable surface defects. Trotz, in Patent No. 705721, further pointed out that if the metal is permitted to splash into the mold the splattered metal will adhere and the casting will be full of blowholes and pipes. He attempts to overcome this difficulty by pouring the molten metal into a funnel that extends into the mold and into the molten metal.

More recent patents—for example, the Betterton et al. Patent No. 2195809—point out that the head of the metal must not exceed a certain maximum; in addition, turbulence must be avoided. For if the head of molten metal above the metal solidfying in the mold is too deep, the freshly solidified skin will rupture in numerous places, imparting a rough, undesirable surface to the congealed metal. In the extreme, the casting may even break in two.

The surface of the mold where the molten metal first enters must be smooth and free of scours and pits, otherwise the very fragile skin that first forms might adhere at such points or flow into the surface imperfection of the chill surface. One can appreciate that the mold wall, even when it is smooth and free of undesirable defects, may disintegrate with time, unless the surface is protected in one way or another from the intense heat and frictional movement of the casting. Therefore, one of the problems is to develop a surface that will remain smooth and free of defects over a reasonable period of time.

The pinch rolls must be designed so that the casting will not slip as the casting is withdrawn from the mold at a uniform rate. They must not distort or impart undesirable markings to the surface. The metal must be congealed to the extent that the pinch rolls will not deform the casting, permitting the partially liquid interior to break through.

Overheating of the pinch rolls and the surface of the metal is prevented by continually flooding them with water (since a considerable temperature gradient exists between the interior and surface of the casting as it leaves the mold, the surface will experience a considerable increase in temperature unless further cooling means are provided, and it is possible to weaken the surface to the extent that bleeding may actually occur).

The pinch rolls are not used to pull the casting through the mold but rather to guide the casting through at a constant rate. Allowance must be made so that the grip on the casting will be positive at all times should slight variations occur in the cross-sectional area of the casting.

Another important consideration is that the alignment of the pinch rolls must not cause the casting to engage the mold walls with more frictional contact on one side than on the other.

The ingots can be cut to the desired length in many ways. Hot saws have been used, but for steel the cutting lance seems to be preferred. Obviously, the casting must not be cut until it has solidified clear through. The cut lengths can usually be rolled directly.

It appears that methods of continuous casting can become successful only when means are provided to prevent rupture and adherence of the freshly formed skin to the mold wall as well as distortions and disintegration of the mold. The steps taken by the author to overcome this and other inherent difficulties will now be described.

The Goss Process

The author has been experimenting with a stationary mold designed to overcome the difficulties of the prior art, especially, (1) sticking in the mold, (2) distortion of the mold, (3) fracture of the casting as it goes through the mold.

Of all the methods suggested by the prior art, the stationary mold appeared to be the most logical one to use. Its success depends to a large degree upon the expedients devised to overcome the difficulties encountered in the past.

A continuous casting machine to produce 4 by 4-in. billets has been built for experimental operations, at the Duluth plant of the American Steel and Wire Co. (Figs. 12 and 13). So far, only a few casting operations have been attempted and those mainly to eliminate a number of mechanical difficulties. This mold has resisted distortion satisfactorily and in no instance has the metal shown the slightest tendency to adhere to the chill surface. The experimental work has been slow, mainly because of labor shortage and the heavy demands of the war effort on this particular plant.

The structure shown in Fig. 14 illustrates the general construction of the machine used to cast 4 by 4-in. billets. It consists of three principal parts: (1) the preforming chamber, (2) the forming chamber, (3) the lubricated chill plates.

The preforming chamber, into which the metal is teemed, is preheated by suitable means, such as Globar heating elements. Before the teeming operation begins, the preforming chamber is heated to approximately the melting point of the steel or metal being cast. This prevents undue chilling of the metal being poured into the preforming chamber (pouring box), which otherwise might freeze in the runner gate and skull in the preforming chamber.

With the arrangement used here, the molten metal is preformed to the desired shape before chilling begins. This permits the gases to escape and allows the molten metal to attain its maximum density by giving it an opportunity to compact itself. If this were not done, cold shuts, scouring, gas pockets, and many other undesirable flaws would develop.

This preforming chamber meets the requirements suggested by the prior art, notably by Trotz, who was perhaps the first to recognize the importance of introducing the molten metal without turbulence into the mold.

As soon as the molten metal has been properly preformed, it is ready to enter the forming chamber. This is water-cooled, and much shorter than the remainder of the mold. The chill surface of the forming chamber must be absolutely nonwetting to the molten metal that comes in contact with it. To prevent distortion of the chill surface, it is made quite heavy, ranging from ½ to 1 in. in thickness and provided with adequate water cooling to keep the surface at the lowest possible temperature. Copper chill surfaces of substantial thickness are permissible when casting steel, since the thermal conductivity of copper is much greater than that of steel and very little change occurs when copper is heated to 1000°F. The surface is made nonwetting, for example, by impregnating it with graphite. This surface stands up very well and resists fire checking, and the molten metal does not adhere to it when the skin of solid metal forms.

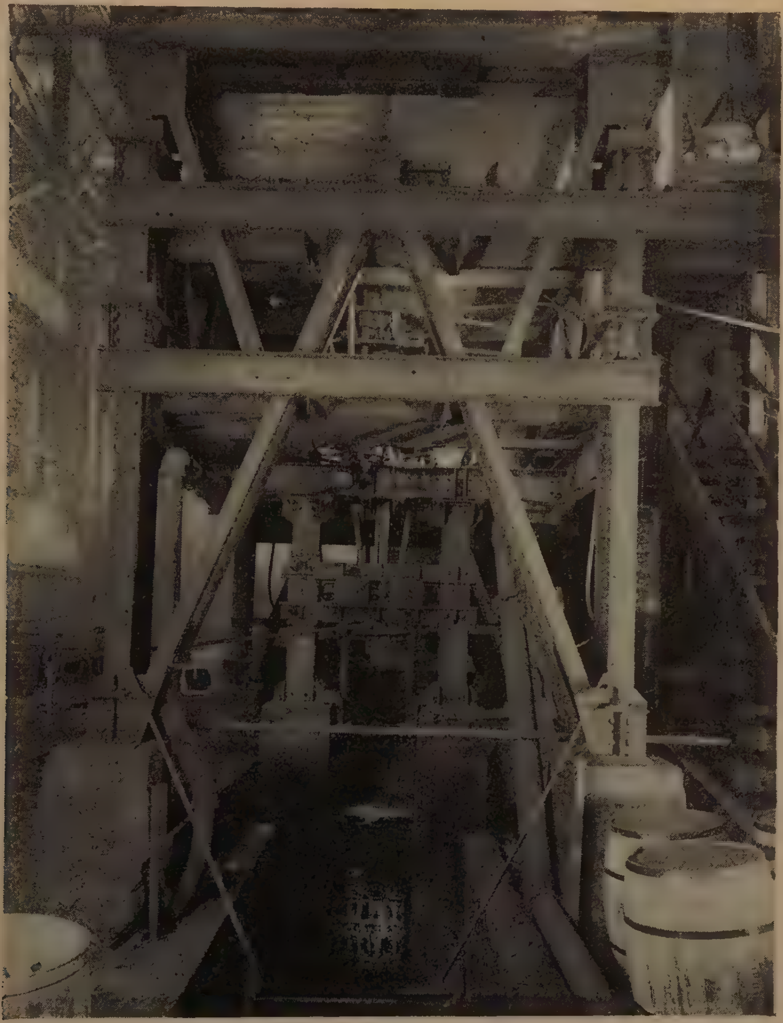

Fig. 12.—Continuous casting machine at American Steel and Wire Company's Duluth Works.

Showing pinch rolls, dummy billet, sectional water-cooled molds, and lubrication feeder ports stationed along walls of mold.

The chilling action should be as drastic as possible, so that the freshly formed skin that encloses the molten metal will be able to withstand rupture as the casting moves through the mold. The skin that first forms is very fragile; it cannot support the molten interior and therefore requires continuous protection against rupture as the billet moves through the mold.

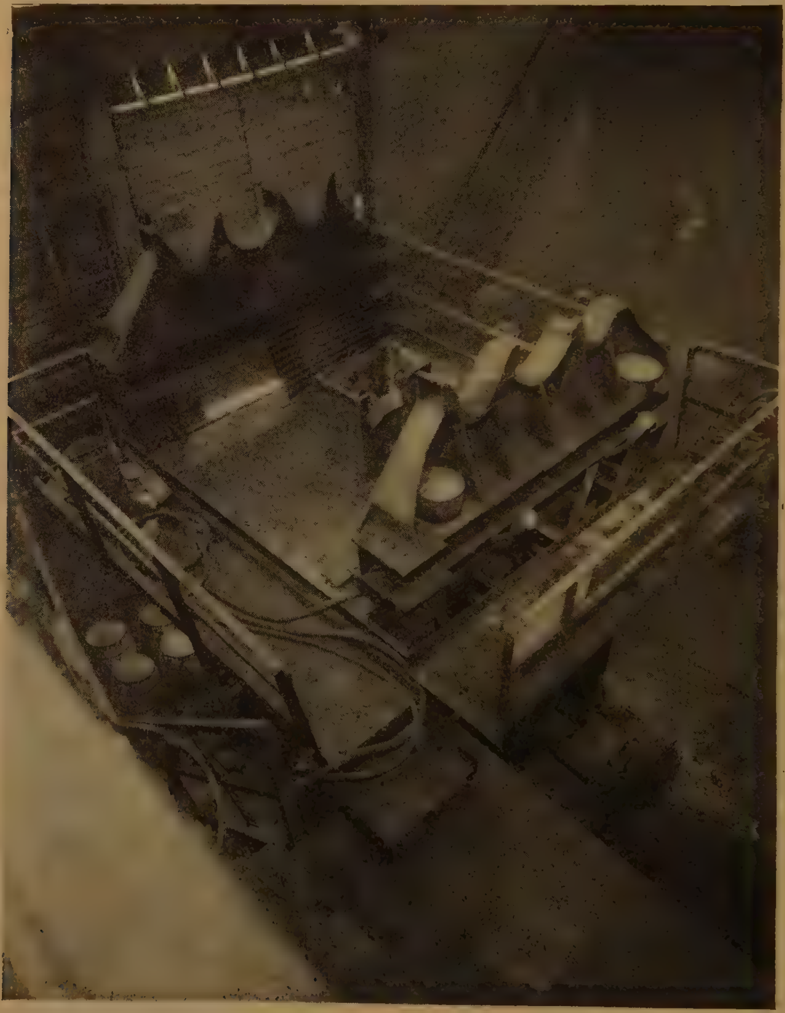

FIG. 13.—SAME MACHINE AS IN FIG. 12, SHOWING POURING BOX.

To facilitate the movement of the casting through the mold, means are provided for lubrication at stations spaced along the side of the mold, in the manner indicated in Fig. 14. The lubricant may be any substance that can be introduced into the mold without disassociating or reacting in a deleterious manner with the surface of the metal going through the mold. In the experiments now in progress, graphite is used and may be introduced either in powder form or as a briquette. If a briquette is used, it must disintegrate into powder when it rubs the surface of the intensely hot billet.

The powder or the briquettes are inserted into the slots in the side of the mold and pressure is applied by the lever system shown. It was found that very little pressure was required to keep the graphite in good contact with the billet going through the mold.

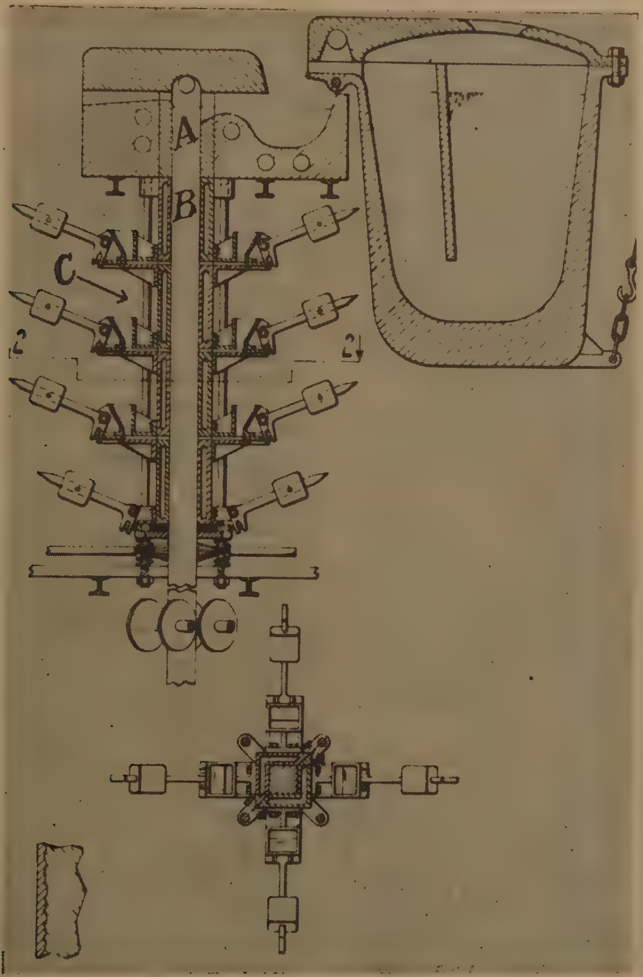

FIG. 14.—GOSS PATENT 2225373.
A, preforming chamber. *B*, forming chamber. *C*, lubricated chill plates.

When a proper head is maintained on the metal entering the casting chamber, the skin formed on the liquid steel tends to maintain substantial contact with the mold wall as it glides by the chill surface. The air gap that forms must be held as small as possible. If it becomes too large, the surface of the billet is reheated by the molten interior and rupture may occur. Bleeding will follow and undesirable surface defects will develop. Also, there is the danger of voids forming in the interior of the billet when this happens.

Even a small air gap is known to reduce the heat transfer appreciably. This can be demonstrated experimentally as well as mathematically. When the chill surfaces are made of copper, they carry the heat away faster than the congealing steel can give it up, especially when an air gap forms.

One function of the lubricant is to provide a self-accommodating material, which readily conforms to the interstices between the metal skin and the chill surface of the mold. Graphite is suitable, because it not only substantially seals the air gap but is a good heat conductor and, being a good black body, absorbs heat radiated from the steel and transmits it to the mold wall without reflecting it back upon the steel from which the heat is received. It further protects the mold wall from direct contact with the surface of the billet, thereby reducing abrasion and scouring and premature fire-cracking of the surface. Another function of the graphite is to reduce the frictional resistance to the movement of the billet through the mold.

The graphite lubricant is applied to the steel only after a solid skin has formed. If the graphite should come into direct contact with the molten steel, it would combine with it chemically and thereby change the analysis. However, the lubricant may be applied as soon as a skin is formed.

A second feeder port supplies additional lubrication to further coat the surface of the billet with a film of the lubricating material, and especially to provide an effective means of imparting a protective film lubricant to the mold walls, thus maintaining good heat transfer. The lubricant is supplied to all sides of the billet.

The number of lubrication feeder ports depends upon the length of the mold. At present they are spaced about one foot apart, in order to properly support the solidified surface and effectively lubricate the mold wall.

When the molten metal is guided through the mold, the chill surface experiences a rise in temperature. This rise is not the same at all points of the chill surface, since it is well known that the metal is continually making and breaking contact with the chill. At the points of contact, the mold surface is undergoing expansion, for the temperature is rising. At points where the air gaps have formed, however small, the chill surface is experiencing a fall in temperature, and contractions occur. The areas of contraction and expansion are continually changing and if they cannot be properly controlled, warping of the mold surface occurs. This is one reason why the air gap must be controlled so that it does not become too large. Copper has excellent thermal conductivity, and therefore is capable of quickly dissipating heat concentrations at localized points, provided the temperature gradients on the surface of the chill surface remain small.

The mechanical stresses set up by the temperature gradients in the chill surface are resisted by a substantially heavy chill surface. However, it is likewise important that the water cooling be uniform throughout the entire extent of the mold.

The mold design illustrated in Fig. 14 has been found capable of preventing distortion that would interfere with the operation of the mold. This design was found suitable for 4 by 4-in. sections. The mold consists of a number of short, strong sections, each water-cooled separately, in order to assure uniform cooling of the chill surface.

The contractions and expansions that take place during the casting operation are not subject to undue constraint. The slots in the side of the mold permit each mold section to undergo dimensional changes without constraint, and these fluctuations are not transmitted from one section to the other, since the graphite in the slot will yield to these forces. Therefore, the slots stationed along the side of the mold not only provide a means for introducing the lubricant into the mold but also accommodate the dimensional changes that must take place in the mold sections during the casting operation. This design, therefore, not only prevents sticking or adherence of the skin to the mold surface, but also minimizes distortion or warping of the mold.

As soon as the solidified shell of metal is sufficiently strong to support the molten or partially solid interior, the billet is allowed to issue from the mold. Usually cooling is continued by spraying water directly upon the surface.

The rate of casting depends upon the length of the mold and the cross-sectional area of the casting. The mold shown in Fig. 12 is 6 ft. long.

The metal usually is supplied by a lip-pour foundry ladle provided with a slag bridge and a suitable cover. The lining of the ladle is extra heavy, to minimize heat loss. The lip of the ladle is also preheated with a suitable heating means, such as a Globar heating element. With these modifications, the metal can be held molten for a reasonable time and teemed at a very uniform rate. In continuous casting, it is very important to supply the metal to the mold at a nearly constant rate, so that a constant head of metal is maintained in the pouring box.

To start the casting operation, a dummy billet having the same dimensions as the billet to be cast is placed in the mold and moved to the top by means of the pinch rolls. The metal is teemed into the preforming chamber and the downward movement of the dummy billet is started. When the dummy billet passes through the pinch rolls, it is disconnected. The billets are cut to the lengths desired by means of a cutting lance.

The metal leaving the mold will have a temperature above 1900°F. Further cooling is accomplished by spraying water directly on the casting.

Metallurgical and Economic Aspects of Continuous Casting

Casting molten metals continuously into billets, slabs, or other forms of relatively small cross section gives one the advantage of being able to solidify the metal at the most rapid rate possible. When molten metal is transformed directly into a slab ingot or billet in a continuous manner, under precisely controlled conditions, many of the present-day difficulties can be minimized, especially segregation and lack of uniformity.

Rapid solidification of the molten metal gives the smallest grain size and less segregation. W. J. Priestly[4] studied the effect of rate of solidification in ingot molds and found that steel that was rapidly chilled responded more easily to heat-treatment. While forging or hot-rolling may improve the structure of metal solidified slowly in the mold, the deleterious effects of segregation can never be removed. He also found that the most uniform structure was produced when the metal was cast in a conventional mold from a temperature but slightly above the melting point. When cast in this way, the metal should be tapped from the furnace at the highest possible temperature, to permit the occluded gases and inclusions to rise to the surface of the melt. These are removed by allowing the steel to remain in the ladle for a time, thus permitting the gases and inclusions to leave the melt. When sufficiently cool, it is cast as rapidly as possible.

While substantial improvements[5] have been made in the casting technique, the ultimate can never be attained in the conventional mold. It is for this reason that more and more attention is being devoted to the development of continuous casting methods.

The transformation of the metal from the liquid to the solid state involves a tremendous change in the heat content. In the conventional mold this is a time-consuming operation, and, because of the great variation in the rate of solidification from the surface to the center, gives rise to ingotism, segregation, and dendrites of all sizes.

In continuous casting the ideal rate of cooling can be more nearly approached and the resultant structure is remarkably free of the defects developed by slow solidification. The rapid chilling prevents segregation of the inclusions.

One of the fundamental aims of the steel and nonferrous industries is to produce ingots of improved quality, and the ultimate can only be achieved by continuous casting methods.

The patent specifications pertaining to continuous casting show that these methods were devised to improve the structure of the casting. This was especially true of the early patents on the subject. This is now taken for granted and nearly all the recent patents describe ways and means of overcoming the inherent difficulties of the method.

In some patents the method was developed to eliminate the blooming mill, soaking pits, ingot molds, or other equipment. These represent an important capital investment. The principal operating costs, including labor, powers, fuel, and scrap losses, represent an important part of the total production cost. To justify the operation of a blooming mill, large tonnages must be rolled. Reasonable operating costs are obtained when 50 to 100 tons per hour is rolled. Mold replacements to cast 60,000 tons of steel cost about $15,000.

From the work the author has done, it is quite apparent that the continuous-casting equipment will be of the simplest construction; in fact, as the various parts are reduced to their simplest form, operation has always improved.

In view of this trend, it would be reasonable to assume that the cost of the continuous casting machines will be reasonable. The money that has been invested in a single machine is certainly high but most of it represents changes and experimental costs.

Once continuous casting becomes acceptable, decentralization of certain branches of the steel industry will be possible. Small plants can then be distributed with regard to market, raw materials, electric power, coal, and labor. In time of war, this is highly desirable, as bombing of widely distributed steel industries is most difficult and small plants are easy to conceal.

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DISCUSSION

(*Carl E. Swartz presiding*)

THE CHAIRMAN.—Thank you, Mr. Goss. Gentlemen, I believe we have heard one of the finest papers, especially since Mr. Goss has been very generous in his frank discussion of continuous casting. One point he has brought out which I think some of us have not thought through to the same extent that he has—that the continuous casting process offers the small producer an opportunity to compete with the larger, more conventional and presumably better established industries.

The meeting is now open for discussion. Are there any questions concerning the first two papers?

J. A. MALONE.*—I should like to ask Mr. Goss whether there is any special problem involved in the first part, the upper part of the mold before he gets to the first graphite lubricant area.

N. P. GOSS.—You mean in the forming chamber where chilling first takes place?

J. A. MALONE.—Yes.

N. P. GOSS.—So far I have not had any trouble in this part of the setup. My only trouble is in getting the molten steel into the mold. If I can get the teeming operation going without skulling, the casting operation goes on. However, turbulence during the teeming must be prevented. In other words, if air is trapped into the molten metal entering the preforming chamber, it forms an air pocket in the slab or billet, which weakens the section. By the time this part of the casting is ready to come out of the mold, the air pressure is so great that it severs the section as it leaves the mold. In the initial experiments the air pocket due to turbulence was 39 in. long. It looked like a pipe, but was inverted. As the turbulence was gradually cut down, the air pocket was decreased to 6 or 8 in. The teeming operation in the future will be entirely without turbulence, and this will eliminate the air pocket.

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* Lithaloys Corporation, New York, N. Y.

I can say that the structure of the billet above and below the air pocket was excellent.

H. S. BLUMBERG.*—Have your experiments been confined entirely to low-carbon steel, or have you also done some work with intermediate and high-alloy steels?

N. P. GOSS.—So far I have used only high-carbon steels. This was the only analysis available. However, from experience, stainless steels would seem to be easier to cast, in that they have a lower melting point and a greater solidification range. Both of these factors are helpful.

H. S. BLUMBERG.—How about steels that air-harden and tend to crack?

N. P. GOSS.—Such steels would require careful study; i.e., the rate at which the heat may be removed and the temperature of the metal coming out of the mold. However, it would seem that if the metal coming out of the mold is hot enough, no trouble along this line should occur.

THE CHAIRMAN.—A number of interesting points have occurred to some of us who have been studying continuous casting; such things as atmosphere have hardly been mentioned today—such things as gas content. Mr. Lippert, I believe, mentioned that the Eldred process will give dense metal because there is ample time for slow solidification and thereby gas will not be entrapped. I suspect that that is true for certain types of gas, but for gases that are soluble and precipitate only during solidification, it may be somewhat questionable.

Mr. Goss brought out some interesting figures on temperatures.

The matter of cooling is recognized, of course, by all of us as extremely critical.

Production rates have been mentioned. Very little has been said about grain size, dendrite orientation, except in the remarks in discussing the Poland process vs. the Eldred process. In one case, you may recall, the heat is withdrawn from the previously solidified rod, making dendrite orientation parallel to the direction of casting movement; in the other, radial dendrite orientation occurs, owing to the removal of the heat from the mold itself. So there are two distinct methods there, both of which are used—at least, I have seen experimental work where most of the orientation was in either one or the other direction.

Mr. Hazelett will present his paper and will be followed by Mr. Valyi and Mr. Williams.

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* Chief Metallurgist, M. W. Kellogg Co., Jersey City, New Jersey.

Improvements in the Direct Rolling of Strip Metal

By C. W. Hazelett*

This paper is a résumé of some of the accomplishments in direct rolling of strip from molten metal, and a description of some experimental developments in recent years.

In all the early developmental work, we used a pair of rolls with a bath of metal between them, maintained by flanges or plates at the ends of the rolls. These flanges produced an excess cooling of the metal and built up enormous pressures at this point as the metal went through the bight of the rolls. Many means were tried for compensating for this excess cooling, such as thickening the strip at the edges, heating the end dams directly or by flowing more of the molten metal against them, leaving an open crotch below the end dam and above the bight of the roll, where the excessive pressures built up could be relieved by some of the metal squeezing out at this point, and so forth. All of these helped somewhat to solve the problem, so that very large heats of many metals melting up to 2100°F., having commercially uniform gauges, could be rolled up to 24 in. in width. The rolls were made by mounting heavy rings on heavy shafts, and pressures up to 75,000 lb. per inch in width were used. Cooling of the rolls was generally done by spraying water on the outside surface of the rolls that came in contact with the molten metal. Roll life was commercial with brass, barely satisfactory with copper, and totally impractical with steels.

The greatest difficulty encountered in all this work was caused by lack of uniformity in the product, owing to a folding action in the mill. Those who are familiar with the operation of a rolling mill know that a bar entering a mill moves at a lower speed than the peripheral speed of the roll. However, the metal solidifying from a bath in a direct rolling mill is cast at exactly the peripheral speed of the roll. This results in irregular folding of the metal, some irregular remelting of the previously solidified sections, and it is difficult, if not impossible, in some cases to exert enough pressure to weld these folded sections sufficiently into a sound product. In addition to this melange of solid, semisolid and liquid metal in the bath, we know that pressure near the freezing point of any alloy in which the constituents have different melting points—and I believe all of them have—causes the lower-melting-point constituent to be squeezed back until it becomes cold enough to solidify and go through the mill. This segregates all alloys, the segregation increasing with the pressures and the freezing ranges of the metals. Add to these problems the excessive roll-maintenance costs with high-melting-point metals and then, the greatest difficulty of all, the vanity of *homo sapiens* where a matter of possibly large importance is being considered, and the problems seemed almost insuperable. It was long ago obvious to me that something much more than the size of a corporation's money and self-assurance was necessary if this process was to be made commercial.

I should like to show you first the performance of the only mill we ever really designed and built, to see what might be done with a well constructed mill. We accomplished something new in history with this process, first, by producing at Scovill Manufacturing Co. coils of brass

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* Consulting Engineer, Greenwich, Connecticut.

12 in. wide and up to 2000 lb. in a heat. This metal was segregated, and had stains that limited the uses of the metal considerably.

We produced accurately gauged coils of 2S aluminum, 24 in. wide. (I might say that the amount of metal that can be rolled in one heat has never at any time been limited by anything except the melting capacity available.) Strip metal 24 in. wide was produced directly from molten metal, but the use for this product was greatly limited by the segregation, which was its one difficulty. The engineers on this installation insisted that they could successfully produce steel strip, and, surprising as it may seem, they were able to turn out a very sound low-carbon strip—but, as I had previously learned at the cost of only a few hundred dollars, the roll life was hopelessly impractical.

The steps in solving the problem of the renewal and cost of the cooling surface involve the use of a relatively thin ring on which the molten metal is poured, and the two then travel between a pair of rolls. In both cases, very thin sections of metal are used for the cooling surface, to get rid of the large variations in temperature and resulting expansion and contraction with thick sections. Moreover, in all cases the water cooling is on the opposite side of the cooling surface from that on which the molten metal is poured. Our thermal conditions approximate those in a water-tube boiler in which very high temperatures operate for many months consecutively with water on the opposite sides and with comparatively low pressures.

The cooling surface in our high-speed mill today is just a strip of high-chromium steel, bent into a circle and welded. This is, of course, extremely cheap; it can be even 50 ft. in diameter if desired, and it is safe to say that the cost of cooling surface per ton is less than 1 per cent of that on any previous mill. This mill was so arranged as not to form an appreciable bath and was limited to very thin gauges. The product, however, was still folded and segregated somewhat but not nearly so much as previously. To produce a thicker bar, and to prevent segregation, metal was then poured on the inside of a ring, and pressures about 1 to 2 per cent of those previously tried were used. Heavy bars of pure chilled castings were produced, eliminating noticeable segregation and having only the one disadvantage of very substantial edge scrap.

This left only the important problem of better edge compensation in a mill using bath distribution of the metal. The latter is essential to uniformity of distribution and, therefore, to wide strip.

Considering the tremendous possibilities of this process if all these difficulties could be answered in a single design, and having worked the problems out separately, I have felt that further perseverance in this research was worth while, and although I have given a large part of my time to what I believe is a far more important, though nonremunerative invention, I have quietly continued my efforts in this interesting field.

I have recently built and tested a mill on low-melting-point metals, which produces very thick or very thin gauges with pressures and horsepowers of 1 per cent or less of those heretofore used, with enormous increase in cooling capacity and decrease in cost of the cooling surfaces, with bath distribution indicating that any width of metal that can be handled can be rolled, and which has, as the solution of the most difficult problem of all, perfect compensation at the edges of the mill. The latter has been exceedingly important because the slightest excess cooling at the edges produced pressures that exceeded the allowable pressures to prevent rolling, folding and segregation, and with insufficient cooling at the edges, the bath always floods through, preventing the operation of such a mill. It now seems reasonable to assume that commercial widths and thicknesses of any metal that is fluid and clean will be produced in the future by this process.

Commercial tests on steels will be made on this mill this spring, and I may report results therefrom at a later date.

The Soro Process

By E. I. Valyi,* Member A.I.M.E.

The purpose of the continuous casting processes is twofold:

As the name implies, they aim at performing a heretofore intermittent operation continuously; in this respect, they tend to satisfy the appetite of the beast that modern extrusion plants and rolling mills have grown to be. The effort invested in the development of these methods bore rich dividends in economy and in the improvement of technical characteristics.

The other purpose of many continuous casting methods is to reduce the number of operations mushrooming between the liquid alloy and the finished mill product, essentially by substituting adequate chill in comparatively small cross sections for one or more "breakdown" steps.

It is this second tendency of continuous casting that justifies description of the Soro process within the frame of our symposium: although not continuous, the Soro method constitutes a means of converting molten metal into a nearly finished mill product.

The Process

The name, Soro, is a composition of initials and abbreviations, with no particular technical significance. The process originates in Switzerland; it was adopted by numerous European plants between 1937 and 1940 and is now being installed in this country. It is applicable to ferrous and nonferrous alloys of an exceptionally wide range of composition. It is capable of producing rod from ½ in. to approximately 4 in. in diameter, or other simple solid shapes of corresponding cross-sectional area.

Fig. 1 shows schematically the succession of operations involved. A ring is cast in a two-part centrifugal-casting metal mold. The cross section of the ring may be round, hexagonal, rectangular or some other solid shape, with the exception of any contour that is undercut with reference to the mold parting line. As cast, the ring has a riser along its inner periphery, which is removed in the next operation, so as to leave the ring with a clean cross section. Following the removal of the riser, the ring is severed at one point and one end is bent outward, leaving a slight clearance between the two ends.

The next step is straightening of the ring in a special device, forming a bar with a slight bend; this is followed by any one of the conventional finishing operations that are necessary to obtain forging rod, screw-machine stock or strip.

The outstanding features of this procedure are:

1. The cross section cast is the same or within a few per cent of the cross section of the finished product (except for fabricating into strip and wire).

2. All operations following casting of the ring are performed cold.

Equipment

The equipment required is simple and inexpensive. The casting machine is a conventional horizontal-shaft mold assembly, similar to those found in centrifugal-casting foundries. Fig. 2 shows a battery of three machines with their protecting hoods swung open. One of these machines,

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* President, A. R. D. Corporation, New York, N. Y.

with the cover closed and pouring taking place, is shown in Fig. 3.

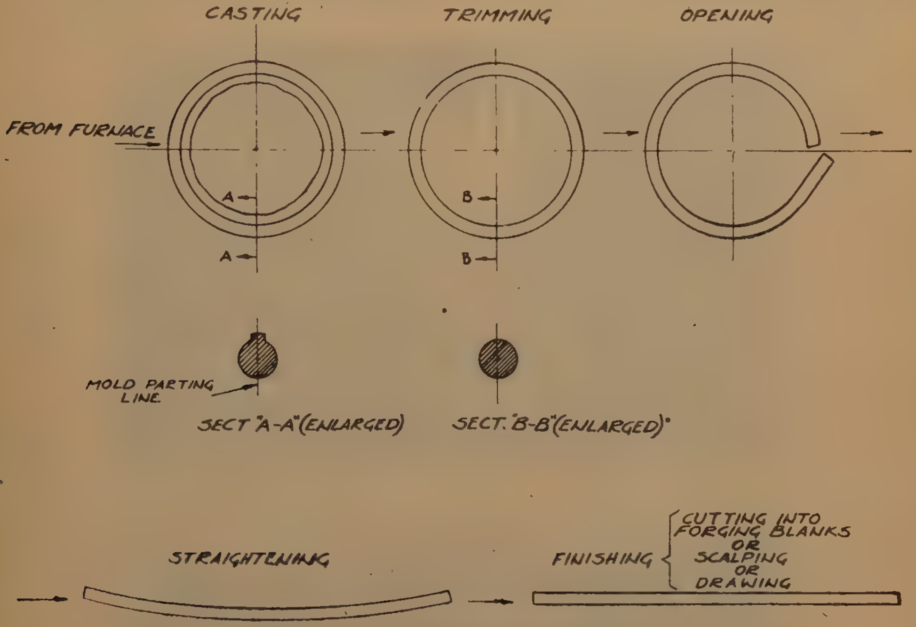

FIG. 1.—OPERATIONS IN SORO PROCESS.

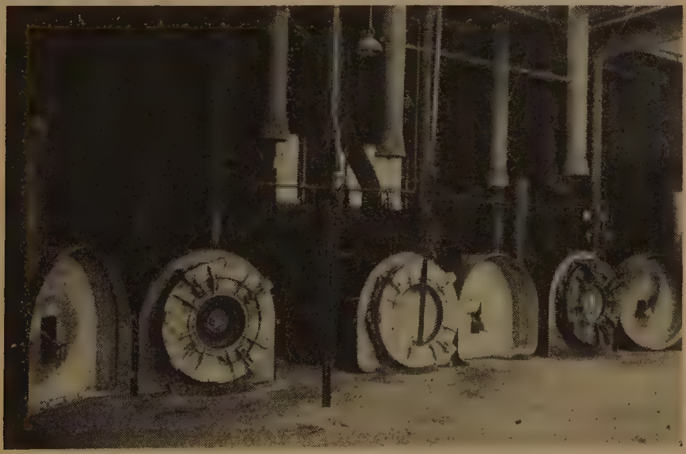

FIG. 2.—SORO CASTING MACHINES.

In Fig. 4, the casting is being removed from the die. The pdie roper is inserted in the fixed and detachable holders. Usually it is made of cast iron, of a grade suitable for permanent molds.

The riser can be seen on the casting in Fig. 4. This riser contains all impurities that are displaced toward the inner periphery by centrifugal action; it also serves as a shrink head, to ensure adequate density in the casting proper.

Trimming of the casting can be carried out on any standard boring mill or lathe. Opening of the ring is a conventional operation, requiring a saw and a small crank press, or a machine that combines the cutting and bending means in one unit. Straightening is the only operation that calls for a special attachment, to be used in conjunction with a conventional straightening device, such as a roller straightener or a drawbench.

Fig. 5 is a schematic representation of the straightening process, as adapted to a standard drawbench. The opened ring is set in place on roller guides. The bent end is pushed through a die and clamped in the vise. The die serves mainly as a guide and does not impart any reduction in cross section to the ring. As the pull is applied, the inner periphery of the ring is cold-worked immediately before the die by means of a hammer, or by rollers. Because of its simplicity, the hammer is usually given preference. This phase of the operation is called pre-compressing.

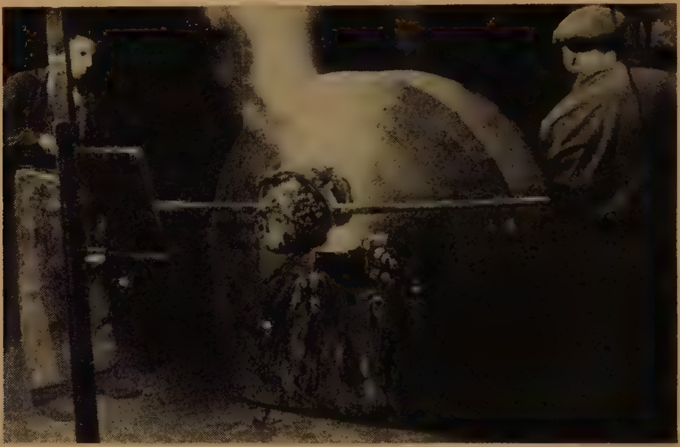

FIG. 3.—POURING IN SORO PROCESS.

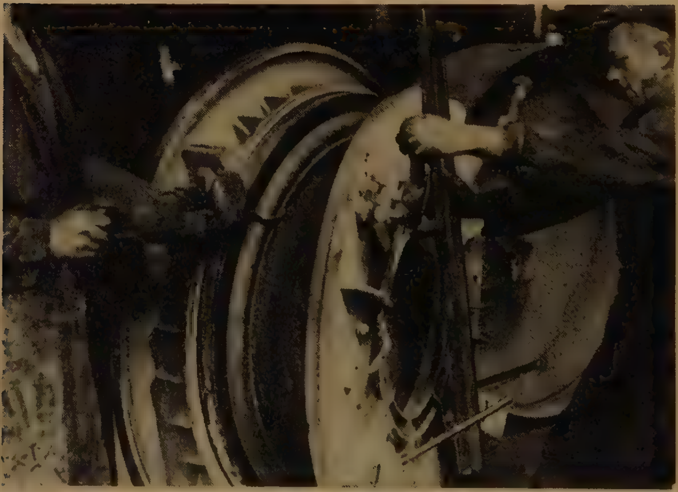

FIG. 4.—REMOVING CASTING FROM DIE.

Fig. 6 is a schematic view of the die and hammer assembly. Rolls can be substituted for the hammer if the span between the "inner" roll and the die is short enough. The hammer is simpler to adjust and to operate; its advantages are particularly noticeable in handling brittle alloys and heavy cross sections.

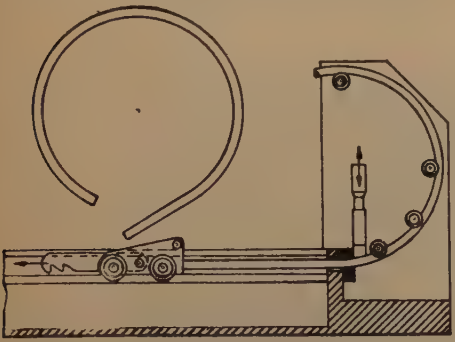

Fig. 5.—Straightening process adapted to standard drawbench.

Fig. 7*a* shows a drawbench equipped with a hammer driven by electric motor; Fig. 7*b* shows a close-up of the die end and Fig. 7*c* the condition of the bar after the straightening operation. Further fabricating depends on the ultimate use of the bar.

Fig. 7.—Fabrication of bar.
a, drawbench with electric hammer.

For the production of screw-machine stock, the bar is given a pass through a roller straightener, then pulled through a scalping die, to remove the cast skin, and finally is given a sizing pass in a drawbench. If die-forging blanks are to be made, it is usually sufficient to cut the blanks from the straightened bar, although a scalping operation may be advisable occasionally.

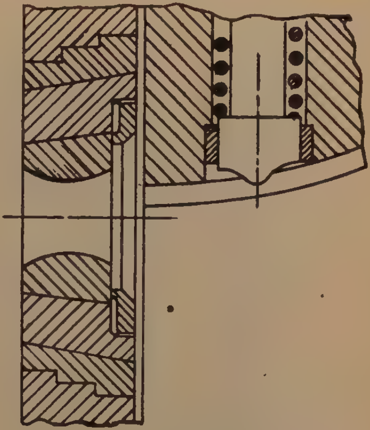

Fig. 6.—Die and hammer assembly.

If strip is to be rolled from the bar, no further operation beyond straightening is called for prior to cold-rolling.

Technique

Casting and straightening are the critical operations. In casting, the amount of chill must be adjusted to the alloy and to the cross section of the casting. In order to obtain the required density, uniformity of structure and smoothness of surface, the speed of rotation and the rate of pouring must be controlled. In the straightening operation, the speed of pull must match the rate and amount of precompressing for any given alloy and cross section. The speed is well within the range of standard drawbenches.

Precompressing is necessary mainly for two reasons:

1. It permits the use of high speeds, such as are customary in conventional drawing operations.

2. It prevents the occurrence of hairline cracks and other, more serious, defects in straightening. The initial jolt at the start of straightening will do no harm to the casting.

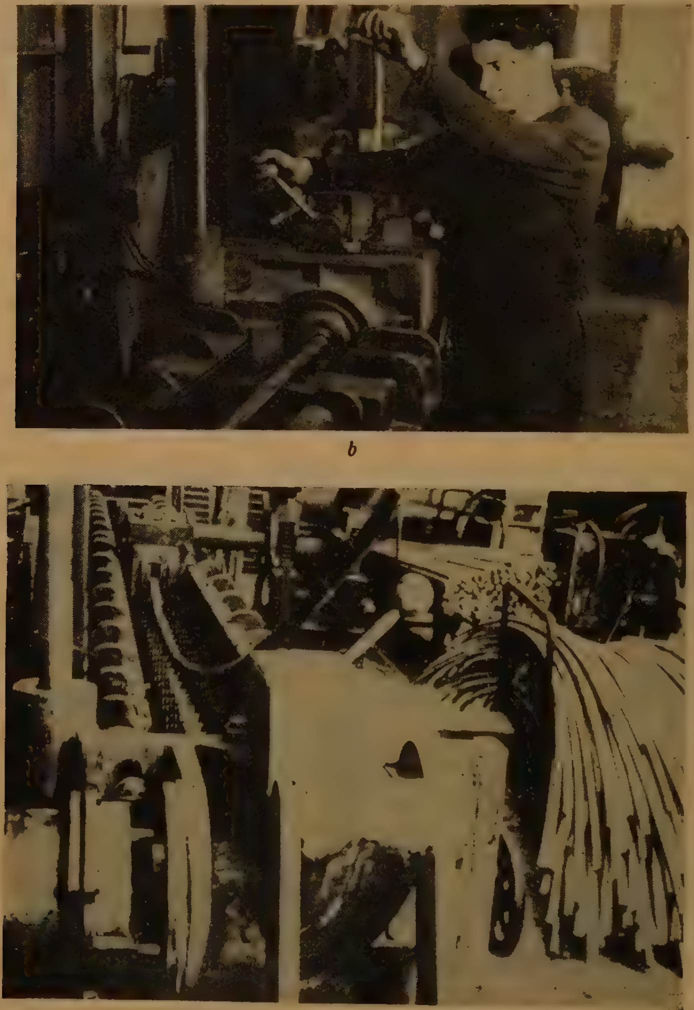

FIG. 7.—FABRICATION OF BAR.
b, die end.
c, condition of bar after straightening.

Many methods of straightening were considered and tried. The experiments included hot straightening, direct bending, stretching and rolling. It was found that the Soro method is the most versatile, affords the greatest speed with a minimum of special skill and requires the least amount of equipment and labor.

PROPERTIES OF PRODUCT

The product is of high quality and easy to control. Composition is uniform throughout the bar.

Centrifugal segregation, sometimes encountered in heavy-walled sleeve bearings and similar centrifugal castings, is avoided, since the difference in centrifugal force between the inner and outer peripheries is negligible, and because of the rapid chilling of the casting.

The bar compares favorably with its wrought counterpart as to physical properties. Tensile strength and elongation will be within a few per cent of the figures applicable to rolled or extruded material. If used for forging blanks, the lack of wrought texture will be of great advantage.

APPLICATIONS

The Soro process is not offered as a substitute for extrusion and rolling, but as a supplement. The expense for equipment and maintenance of a Soro installation is very low. Change from one alloy to another, or from one size to another, can be accomplished within a matter of minutes.

A large mill, equipped with modern rolling and extrusion equipment, will find the Soro process useful for taking care of orders calling for special alloys, fast delivery of odd sizes and for small quantities that are difficult to schedule.

The small plant will find the Soro process an easy means of producing rod without going to the expense of installing extrusion presses and rolling mills.

Users of large quantities of rod and barstock can take advantage of the process for recovery of plant scrap.

All of these applications connect the Soro process with alloys currently available as rod and forging stock. More important, and of greater potentialities to industry, however, is the fact that the process is not limited to alloys readily workable at elevated temperatures. Hot-shortness and hot-brittleness do not prevent, or even render difficult, the fabrication of an alloy into barstock. Seams, pipe, certain segregations, and other defects originating from the ingot, are eliminated; therefore alloys that have a strong tendency to exhibit such defects are of interest for Soro production.

So far, a great variety of brasses and bronzes, a number of aluminum and magnesium alloys and stainless steel have been fabricated successfully. Many typical foundry compositions can be made available as barstock.

SUMMARY

It is felt that the Soro process will help to supply industry with bars and rods made of alloys not now available in those shapes.

It will make good use of secondary metal and scrap. It will offer advantages in operation, owing to the simple equipment involved, and because the manufacturing units can be adjusted to changing production requirements at any time at low overhead cost.

The Williams Process of Casting Metals

By Edward R. Williams*

Continuous casting of nonferrous metals has become a commercial reality. After years of slow and arduous experimentation by a number of independently working inventors, starting with Lord Henry Bessemer in 1865, success has finally been achieved. Nonferrous metals—aluminum, copper and brass—extremely vital to our production of war equipment, are being continuously cast every day in large quantities. In fact, some nonferrous metals—for instance, high-strength aluminum alloys—could not have been produced in the huge quantities required for planes and other war equipment if it were not for continuous casting. These casting processes for nonferrous metals have not been entirely perfected but continuous casting is here to stay.

Continuous casting of carbon and alloy steel has not yet gone into commercial production but it is well on its way. A great deal of hard work has been expended and small fortunes in money have been and are being spent in marching down the long road to success. Considerable tonnage of plain carbon, stainless and other alloy steels of high quality have been produced by pilot-plant continuous-casting units and at speeds that give indisputable evidence of commercial success.

What has made the difference between failure and success? What is there left to do to revolutionize completely the method of casting metals, which has existed for centuries? These questions are being rapidly answered.

Fundamental Methods

Present continuous casting processes have many common problems but differ considerably in their methods of solution. The two fundamental methods are:

1. Forming the solidifying metal against mold walls that move with the metal, so that there is no relative movement between the walls and the metal. This is a development of Lord Bessemer's idea of pouring metal between two rotating rolls.

2. Moving the solidifying metal along a stationary mold wall so that there *is* relative movement between the wall and the metal. This was proposed by Trotz in Germany as far back as 1889.

Neither Bessemer nor Trotz achieved commercial success. The chief reason seems quite apparent today, inasmuch as they did not solve the fundamental problem of rapid heat removal from the molten metal.

The Williams Continuous Casting Process is based upon this fundamental idea of fast heat removal and dissipation. The bessemer method of forming the ingot against a moving mold wall—either rotating rolls or endless moving plates—was carefully considered by the author and promptly abandoned as being commercially impractical. Primarily, only a very small tonnage output was possible except at terrific lineal speeds, because the very nature of this method required casting thin sheets rather than ingots. Secondly, the casting of a sheet between rolls that are pressed together meant the rolling of two layers of solidified skin separated by a molten core. Internal bursts and segregation of the metal usually resulted.

Moving Solidifying Ingot Along Mold Wall

It was decided therefore to devote our research activities chiefly to the idea of moving the solidifying ingot along a stationary mold wall. It was soon dis-

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* Williams Engineering Co., Latrobe, Pennsylvania.

covered that to obtain commercial usage of this process, particularly in casting steel and other metals of high temperature or heat content, the mold itself must become an extremely efficient heat exchanger. Heat had to be removed from the molten metal almost instantly upon its contact with the mold wall to solidify a "skin" of metal. This skin needed enough strength to prevent rupture while moving along and against the frictional resistance of the mold wall. This required much faster heat transfer than had been contemplated in the prior art; first, from the molten metal to the mold wall, then through the mold wall, and finally, dissipated from the mold wall. Another idea was to minimize both frictional resistance and insulating film between ingot skin and mold wall.

One of the principal features of this process makes it possible to cast metals, particularly steel, at high lineal speeds by the use of a relatively shallow cooling passage surrounding the mold wall. Water or other cooling fluid is passed at high velocity along the outer surface of the mold wall, which effectively "scrubs" the heat away from the wall. This fast removal of heat in turn lowers the temperature gradient through the mold wall and compels a faster flow of heat from the molten metal. The result is an increase in speed of formation and thickness of the ingot skin, enabling it to be drawn along the surface of the mold at higher speeds without rupture. The first test of this discovery raised the lineal speed of an aluminum ingot from about 4 to about 28 in. per minute before rupture of the ingot skin occurred.

Another desirable feature of this process is the use of lubricating materials continuously applied between the mold wall and forming ingot. One of the functions of these materials is to lubricate the mold wall and thus reduce the frictional resistance against the ingot skin. The lubricating material also accelerates the heat transfer between the ingot and mold wall and affords a further improvement in the lineal speed. Various lubricating materials have been successfully employed and others are under constant experimentation to determine those most suitable.

These discoveries have produced lineal speeds on steel ingots of more than 10 ft. per minute. Still higher speeds are expected, based upon current tests. By this process, therefore, tons rather than pounds of metal are cast, which makes it commercially feasible, particularly for steel.

LENGTH OF MOLD

Proper length of mold is determined by the ingot speed required, shape and size of ingot and type of metal cast. The mold should be long enough to permit the solidification of only sufficient ingot skin within the mold to prevent the ferrostatic pressure of the molten interior from bursting the skin as the piece emerges from the bottom of the mold. Completion of the solidification process is controllable by water sprayed directly against the ingot surface. When ingots of large section, particularly those of rectangular shape, are cast at high speed, bulging and sometimes bursting of the ingot skin occur when they leave the mold. Rather than increase the length of the mold to overcome these difficulties, support is provided for the ingot as it emerges from the mold. A series of rollers closely spaced and slightly compressed against the ingot prevent distortion and bulging at that point. In addition, this train of rollers compresses the ingot sufficiently to compensate for volumetric contraction during solidification. The usual shrinkage cavity is thereby squeezed out and "piping" eliminated.

Experimental work has been conducted on the solution of these problems for more than 13 years. In small casting units at Latrobe, Pa., aluminum, brass, copper, and lead were satisfactorily cast. Principal attention was focused on the mechanical operation rather than on quality and metallurgical control, but, notwithstanding, many ingots of commercial quality were produced.

CASTING STEEL

Because of its inherent characteristic of fast heat removal, the possibility of casting steel by this process became apparent. A large pilot unit was built and an arc-type electric furnace installed. Many grades of steel were cast, including low-carbon and high-carbon, stainless and other alloy steels. Ingot sections ranged from 4-in. squares to 4 by 8½-in. slabs. Even 4 to 8-in. round steel ingots were satisfactorily cast. While no attempt was made to determine optimum lineal ingot speed, better than 10 ft. per minute was run. The surface of ingots, even stainless, resembled rolled steel rather than the usual cast ingot. The chief consideration was mechanical operation rather than quality. However, many ingots were rolled into sheets, billets and rods by various steel companies, with consistently good reports especially attesting to freedom from segregation.

During the approximately four-year period of experimentation with steel ingots, a small portable unit, casting a 4-in. round ingot, was tested by a brass producer, with excellent results. The necessity for capacity operations on war production prevented testing on a commercial scale by this company.

For some time a large pilot unit has been in operation at the Cleveland plant of the Republic Steel Corporation. Slab ingots, 5 by 10 in., are being produced from steel supplied by the open-hearth shop. An extensive program of development pointing to commercial use of this process is now under way, in which The Babcock and Wilcox Tube Co., of Barberton, Ohio, is cooperating. Carefully planned experiments on improved methods of pouring large tonnage per hour, quality control, cutting ingots to length continuously, and other factors of commercial use, are in steady, daily progress of solution.

Rapidly mounting interest in this process is being evidenced by ingot producers in many foreign countries. Recently this interest has reached the point where negotiations to grant licenses in a number of these countries have begun. Manufacturers in foreign countries are even more "continuously casting minded," especially in steel ingots, than producers in the United States.

PRINCIPAL ADVANTAGES OF WILLIAMS PROCESS

Many of the details of operation of the Williams process have already been described in patents and trade publications, particularly in *Iron Age*, April 4, 1940, and in *Steel* April 8 and Dec. 9, 1940. Some details are not yet ready for disclosure. Important facts, however, are briefly outlined herein.

The most striking comment by observers is the relative simplicity of the process. Water-cooled molds are used in which the mold wall is relatively thin, usually ¼ in. or less, and made of high-conductivity metal such as brass or copper. However, quite thin mold walls, 1⁄32 and 1⁄16-in. metal, and also mold walls of steel and other metals, have been used successfully and ultimately may be made to accelerate heat removal.

Water requirements for the mold so far have been about 100 gal. per minute or less and spray water has been about 200 gal. per minute. Water pumps of moderate size can be used, therefore. The rise in temperature of the water under conditions of present operations with steel has been less than 50°F. Passage for cooling water surrounding the mold wall has been made as shallow as practicable, considering the factors of pressure differential between inlet and outlet but striving for maximum velocity along the surface of the mold wall.

Power-driven pinch rolls beneath the output end of the mold pull the ingot from the mold at a predetermined speed. Motor drive for pinch rolls has ranged between 5 and 25 hp., depending on ingot size.

Cutting-off mechanism for steel ingots consists of oxyacetylene torches synchronized with the moving ingot, which rapidly cut it to desired lengths. Nonferrous metals may be cut to length by a traveling saw or similar equipment, or pouring may be stopped when the desired length of ingot is reached, and the process repeated.

Usually only three operators are needed to handle pouring, speed control and cutting of the ingot and probably two of these operations will be made fully automatic on a commercial unit.

Almost the only present difficulty in casting steel ingots is in preventing the steel from freezing in the nozzle of the pouring box. When casting ingots of small cross section, such as 4 in., it has been necessary to use nozzles of ¾-in. diameter or smaller, to avoid extremely high lineal ingot speed. With larger ingot sections or higher ingot speeds, nozzles of larger size can be used, which will eliminate this problem. Experiments are now being conducted in which pouring box and nozzle are being controllably heated to high temperatures, which indicate the probability of using small nozzle sizes without difficulty. This will make possible the casting of ingots of very small cross section with a minimum of final rolling.

Advantages of this process, especially in casting steel ingots, include: elimination of rough forming and breakdown rolling operations; practically 100 per cent ingot yield of the metal poured; reduction in ingot surface imperfections; elimination of segregation and improvement of internal quality of the ingot; metallurgical control of grain size and structure by regulation of cooling speed; and reduction in invested capital per ton of metal cast and rolled.

The Williams process is adaptable not only to the continuous casting of ingots but also to the casting of single-length or stationary ingots in water-cooled molds of similar design. Several years have already been spent in the development of this method. Ingots of brass and steel of various grades and ingot sizes have been cast successfully. Higher ingot yields, metallurgical control of ingot cooling, fast turnover of mold equipment and other outstanding advantages have already been reported. Details are not yet available, but several steel producers are carefully studying the possibilities presented.

Yes, the casting of metals in water-cooled molds, both continuously and in single length, is here to stay.

Conference on Production and Design Limitations and Possibilities for Powder Metallurgy Parts*

(New York Meeting, February 1944)

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* Issued as T.P. 1788 in METALS TECHNOLOGY, January 1945. The Committees in charge of the first Conference appeared also in that number.

Foreword

In one form or another, the art which we now call Powder Metallurgy has, for many centuries, been included among the skills of the metal worker. Before the melting of steel became practical, to cite a single example, steel swords were being fashioned directly from sponge iron by means essentially similar to those now in use for the fabrication of machine parts from iron powder. Modern demands for more materials having special characteristics, not attainable by casting or plastic forming alone, have stimulated the wider application of the methods of powder metallurgy.

Early in the present century the need for a better electric lamp filament was met by the tungsten filament made directly from powder. This development emerged from long and painstaking laboratory research which added much to both the "know how" and "know why" of powder metallurgy. Succeeding advances that have brought forth such useful materials as cemented carbide alloys, porous bearings, heavy duty electrical contact alloys and precision machine parts have likewise added to our store of knowledge of the subject. Yet, it is generally acknowledged that both the practice and theory of powder metallurgy are in their infancy.

New applications and further developments in this field are, of course, to be anticipated; but, the rate of advance will almost surely depend in large measure upon the number of people actively interested and upon their individual and collective understanding of the possibilities, limitations and problems inherent in the process. In the promotion of more widespread interest as well as in furthering general understanding, open discussion, either through the literature or in technical assembly, can serve a highly useful purpose. The research man, to a large extent, relies for his guidance upon the needs expressed by the practicing engineer. Free interchange of ideas not only increases the sum of knowledge, but also serves to stimulate creative thought. It is a common experience that the very act of setting down one's thoughts for the consumption of others tends to crystallize nebulous ideas, to bring into clear focus principles that have long lain concealed in a camouflage of detail.

Until recently there have been but few and sporadic attempts to bring the powder metallurgists together in technical discussion. These have been useful, however, in breaking down the wall of reserve that inevitably surrounds any field of technology that has developed more as an art than as a science and have cleared the way for more open and beneficial intercourse. Recognizing the need for an organization to sponsor a continuity of discussion and publication in the field of powder metallurgy, the Executive Committee of the American Institute of Mining and Metallurgical Engineers, at its April 1943 meeting, authorized the creation of a standing Committee on Powder Metallurgy. Subsequently this committee was adopted by the Institute of Metals Division as one of its special committees.

At its initial meeting, under the chairmanship of Mr. Fred P. Peters, the committee agreed, as an experimental procedure, to hold a one day conference, patterned after two earlier symposia held under the leadership of Dr. John Wulff at the Massachusetts Institute of Technology. Papers were invited for a morning session on the practical subject "Design Factors in Powder Metallurgy" and an afternoon session on fundamental research in powder metallurgy. The conference was held on Monday, February 21, 1944, and was attended by more than four hundred members and guests of the Institute. This issue of METALS TECHNOLOGY contains the papers and discussions presented at the conference, preserved in this form as a permanent record of the proceedings.

The committee extends its special thanks to the authors of the papers, to those who participated in the discussion, and to Dr. John Wulff, who acted as general chairman of the conference.

FREDERICK N. RHINES, *Chairman*,
Subcommittee on the Publication of
the Conference Papers.

The Conference

The First Conference of the Powder Metallurgy Committee convened in the East Foyer of the Hotel Waldorf-Astoria, New York City, at 9:45 a.m., on Feb. 21, 1944, Mr. John Wulff, General Chairman, presiding.

THE CHAIRMAN.—In behalf of the American Institute of Mining and Metallurgical Engineers I welcome all members and guests to this conference on Powder Metallurgy.

We hope that this meeting will give expert and novice in the field a chance for discussion. Unfortunately, the subject has been overemphasized by some, and, of late, severely criticized by others.

We have here today powder producers, fabricators, and engineers of different viewpoints, who can make the meeting a success. Such success depends not only on the caliber of the papers presented but more so on the discussion. To give you time for a free exchange of views, the papers have been shortened purposely.

With the hope that you will all benefit by this conference, I shall turn the meeting over to the Chairmen of the morning session, Mr. Roland P. Koehring, of Moraine Products Division of General Motors, and Dr. R. K. Waring, of the New Jersey Zinc Company.

The subject of the morning session was Design Factors in Powder Metallurgy and the opening paper of the session was presented by Mr. Fred P. Peters, as follows:

Design Factors for the Metal Forms with which Powder Metallurgy May Compete

By Fred P. Peters,* Member A.I.M.E.

At first glance this paper may seem unique among those comprising this symposium on designing for powder metallurgy, since it is evidently concerned with everything *but* powder metallurgy. This paradox will be at once resolved, however, when the real purpose of the symposium meeting is understood—to present factually and objectively the things that can and cannot be done with powder-metallurgy methods, and especially to set forth with brutal frankness the limitations of powder metallurgy, so that costly overenthusiasm and misapplication may be prevented.

Since much of powder metallurgy's future development (and many of its present disappointments) has been in competition with other and long-established methods of fabricating parts, it is easy to see that its true competitive possibilities in any given case cannot be accurately appraised without rudimentary knowledge of what the competition can do. This paper, therefore, presents a few reminders of things you all know—a background to be kept in mind as you examine the data on each of their specialties given by the authors of the papers that follow.

From the standpoint of the design engineer powder metallurgy is often in competition with one or more of the following: sand casting, die casting, permanent-mold casting, precision investment casting, machined bar stock, screw-machine parts, cold-heading, drop-forging, and stamping and drawing. We will here briefly discuss each of these individually, and set forth some rough (and therefore dangerous) generalizations about its competitive position, especially with respect to powder metallurgy.

Sand Casting

Sand-casting of small parts is sometimes an inexpensive method of manufacture, for its raw-material costs (i.e., for gray iron) are the lowest of the various methods and it involves the use of no tools and dies of jewelry quality. Its design flexibility—that is, the ability to make complicated, cored and undercut parts in one piece—is about the highest of the competing processes and in this respect it can do many things that are impossible by powder metallurgy. For small castings its production rates may be higher, by using multi-impression molds, than can be achieved with parts of the same size by powder metallurgy.

But its labor charges for melting, pouring, patternmaking and molding are comparatively high and the waste it entails in gates and risers is always considerable. Tolerances of sand castings are wide (±1⁄16 to 1⁄32 in. per in.) and where precision approaching that of powder metallurgy is required sand castings must be machined to final size, thus increasing their cost. Steel sand castings are more expensive and less precise than iron, and nonferrous the most costly of all.

Manuscript received at the office of the Institute March 8, 1944.

* Editor-in-Chief, *Metals and Alloys*, New York, N. Y.; Chairman, Powder Metallurgy Committee, Institute of Metals Division, A.I.M.E.

DIE CASTING

Die-casting of parts in zinc, aluminum or magnesium alloys has not been greatly involved in competition with powder metallurgy and this is in some ways surprising, since both processes are excellent for large lots, high production rates, close tolerances and minimum waste. But die-casting's raw materials are cheaper than most metal powders, its tool costs—especially for the extended runs for which die casting is generally used—are lower and its production rates for small parts the highest available. Although this may precipitate an argument, re-sized powder-metallurgy parts can generally be made to closer tolerances than the ±0.001 in. common for die castings.

Both have limited design flexibility, but the possibilities of die casting are greater here because the liquid metal will go around corners where a powder will not, and because die-casting dies can more readily embody inserts, slides, several actions and other fancy motions than can powder-metallurgy dies. It appears that powder metallurgy will not be in serious competition with die casting for many years, because of the latter's superior economy for highest production work.

PERMANENT-MOLD CASTING

Permanent-mold casting is in many design respects somewhere between sand and die casting. It is particularly suitable for medium-run work where precision greater than that provided by sand casting but not of the order of die casting or powder metallurgy is required. Tolerances may be held to ±0.005 in. per in. It enjoys more design flexibility than the more precise processes and less than sand casting.

PRECISION CASTING

So-called "precision castings" made by the lost wax or similar investment molding processes, in conjunction with centrifugal, pressure or vacuum casting, have recently increased in importance through their large-scale use for industrial and war products. The method combines the permissible design intricacy of sand casting with precision close to that of die casting (tolerances may be from ±0.005 in. to 0.003 in.). Only one permanent or master mold is required for each design, and production rates may be high. Considerable skilled labor is involved and there is some material waste in the form of sprues. Its best field seems to be the fabrication of small parts to be made of metals whose melting points are too high for die casting, of shapes too complicated for powder metallurgy and of dimensional tolerances too narrow for sand casting.

MACHINED BAR STOCK

Machined bar stock is often regarded as the metal form with which powder metallurgy most often competes. Here more than elsewhere the comparative factors depend on the individual case. The outstanding differences between the methods are that: (1) machining involves considerable waste metal and powder metallurgy virtually none, (2) production speeds are much higher for powder metallurgy, (3) machine time and skilled labor are tied up to a far greater extent by machining, (4) powders, however, still cost a lot more than bar stock, (5) the mechanical properties are usually better for machined parts than for pressed and sintered, (6) design flexibility is much more limited for powder parts than for machined and (7) tool costs are considerably higher for powder metallurgy.

Each design must be considered on its own merits, powder metallurgy being applicable where the first three of the foregoing factors predominate over the last four—and this usually depends on the amount of metal that would have to be removed if the part were to be made by machining. Tolerances are of the same order, machining having an edge. Automatic screw-machine operations, of course, normally surpass powder metallurgy in speed and precision and therefore are beyond competition except for complex shapes that can be made by powder metallurgy and which involve excessive metal removal by machining.

COLD-HEADING

Cold-heading is another process for making small parts of moderately intricate design to close tolerances (±0.002 in.). Its production rates are high, labor charges in the medium range and mechanical quality good. There is virtually no waste metal and excellent finishes usually are obtained. However, wear and tear on heading dies is high, most of the parts require annealing after forming and the process is limited to designs involving upsetting; axial cavities must be machined out. At present it seems to compete most with hot-forging and screw-machine products.

DROP-FORGING

Hot-forging's best-known advantage is the strength and toughness of the metal part. Tolerances maintained are of the same order as those for permanent-mold casting—down to 0.004 to 0.012. This, of course, is wider than for powder metallurgy. Forging involves more waste than powder fabrication but less than sand casting. Tool and die costs usually are high, so that the method is more attractive for long runs than for short.

STAMPING AND DRAWING

Stamping and drawing is a process with which powder metallurgy only occasionally competes for the designer's favor. It is a typically mass production method involving high tool costs, relatively low raw-material costs, medium labor charges and some waste. Very thin parts (thinner than by powder metallurgy or die casting) can be formed to tolerances from 0.001 down to 0.0003 inch.

COMPETITIVE FIELD FOR POWDER METALLURGY

Aside from its special structural or metallurgical possibilities (porosity, oil retention, duplex structures, etc.) it is hard to define exactly the competitive field for powder metallurgy. Perhaps the data to be presented by the other speakers will aid us in approaching such a definition, for it is certainly needed. The problem is complicated by powder metallurgy's over-popularized "glamour," on one hand, and by the fact that recent improvements in powders, press sizes and speeds, coining practices, etc., continually make it possible to reach closer tolerances or higher production rates or better metal quality than was considered feasible a while ago.

Powder metallurgy is, of course, able to accomplish many results and to make possible the manufacture of certain articles, such as porous bearings, tungsten carbide, etc., not producible by other means; but for making ordinary machine parts in competition with other processes, powder-metal men should remember that other fabricating methods are able to do individually some and collectively all of the things that powder metallurgy can do. The fastest production is usually attainable by die casting, the closest tolerances through screw-machine work and the least waste of material through powder metallurgy. Powder metallurgy's tool costs for some jobs are likely to be among the highest. It is in providing just the right combination or compromise that powder metallurgy often shines, however, and we hope to hear many specific details of this nature during this meeting.

DISCUSSION

Roland P. Koehring presiding

T. D. Yensen.*—As my information is of a negative nature, I think it belongs under this paper. We are particularly interested in magnetic materials and we would like very much on occasions to make use of powder metallurgy. We have tried repeatedly to use powder metallurgy in preparing our nickel alloys but always with negative results; that is, we cannot get as good magnetic properties by powder metallurgy as we can by starting with a molten material. We have tried by all possible means to make materials like 50 per cent iron-nickel alloys by powder metallurgy. The compacts can be regularly forged and rolled but no matter what we do in the way of annealing, the magnetic properties come out very much poorer than if we start with molten material.

F. V. Lenel.†—I want to mention one characteristic of articles made from metal powders which distinguishes them from die castings; that is, their wear resistance. Die castings usually are made from zinc or aluminum alloys and a few copper-zinc alloys; all of them are comparatively soft and not very wear resistant. I know of a number of cases where powder metallurgy rather than the die-casting method was used for producing a certain part because higher wear resistance was needed than could be attained in die castings.

A. J. Langhammer.*—The subject of powder metallurgy is somewhat difficult to discuss, and portray, in the time that has been allotted. Most of you would rightly be bored if we went into details. However, I will cite one incident that possibly will help illustrate some of the potentials. Last summer I was in Washington and met Navy officials for the purpose of studying the possibility of making a certain part by powder metallurgy. The part is highly intricate and I happened to remark that the material cost would be high; that is, the cost of the raw material.

Promptly a high-ranking Navy officer said: "Mr. Langhammer, if you must pay x dollars a pound for the raw material, but achieve the desired results, the cost of the finished part would still be low."

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* Research Laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

† Moraine Products Division, General Motors Corporation, Dayton, Ohio.

* Chrysler Corporation, Detroit, Michigan.

Powder Metallurgy as Applied to Machine Parts

By A. J. Langhammer,* Member A.I.M.E.

Broadly speaking, it may be said that the engineer has two major responsibilities: One is to recommend the choosing of proper machinery and equipment; the other, to assist in the simplification of design, determination of method, and advise about the most suitable material to be used.

The products of powder metallurgy enter broadly into both these fields. The oil-cushion, self-lubricating bearing surface on a machine part makes for better machinery and factory equipment, often proves a lifesaver in curing difficulties where bearings are overloaded or inaccessible for lubrication, or on installations that with normal practice constitute a problem entailing frequent repairs. On the other hand, other parts may require low porosity approaching solidity.

In the second field, powder metallurgy provides many possibilities for improved products, improved performance, solving of technical problems, saving of weight, quiet operation, higher factors of safety, greater flexibility, attractive economies, and so on.

Parts

We of the automotive industries are making many powdered-metal war-machine parts, both ferrous and nonferrous, including gears, external and internal; ratchets, both external and internal; levers; pillow blocks; sliding blocks; cams; gibs; hubs with external and internal splines, and similar units. Powdered metals play an important part in our war work, as they did in peacetime in the manufacturing of passenger cars and trucks.

The art of powder metallurgy is not a panacea. Although on certain parts such operations as turning, boring, facing, reaming, counterboring, milling, countersinking, chamfering, broaching, hobbing, profiling, trepanning, gear cutting, grinding, etc., can be eliminated, there will always be the need for machine tools.

Advantages of Powder Metallurgy

Simple machining operations often are eliminated by using powdered metal, and also many other intricate operations, some of which are of the type impossible to perform on the most modern production equipment; for instance, an external spline on a flange hub, where the spline must continue to the flange face and at full depth.

Another important feature is that some of the machine parts may require a self-lubricating surface at one or more points; for example, proper lubrication of a sliding splined spool, while ordinarily most difficult, is accomplished automatically with a self-lubricating powdered-metal bearing.

Frequently machine parts are made with physical, mechanical and technological advantages unobtainable from cast or forged metals of similar analysis. Thus powder metallurgy offers the designing engineer broader latitude. Similarly, the engineer may take advantage of powder metallurgy in his teamwork with other departments.

Another important advantage in powder metallurgy for machine parts is the relatively short time required for tool-up.

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* President, Amplex Division, Chrysler Corporation, Detroit, Michigan.

We have tooled up for a particular job in 24 hr., and the following example is characteristic for a somewhat intricate part. On an internal spline member, we were in production six weeks from the date the order was placed, as contrasted with a nine months delivery promise on a broaching machine and eleven months on broaches. Moreover, our equipment is of special design, making not only for prompt delivery, but also simultaneous volume production.

PARTS ADAPTED FOR POWDER METALLURGY

Generally speaking, the parts that are adapted to powder metallurgy are of shapes that can be cast easily by simple foundry methods and without cores, except for a plain core that would form the bore. These are ideal for powder metallurgy in virtually every respect.

Our policy in making a part from metal powder is just the same as with any other manufacturing problem. If we can make it better and cheaper by using metal powder we will try to do so. If other machinery or methods are better and cheaper, we will not use powdered metal. However, our use of the new art is constantly increasing.

We produce a gear set made from powdered metals, the manufacture of which was considered particularly difficult under ordinary circumstances. We have also made a bronze part for an antiaircraft gun sight, which we produce in a matter of seconds as compared with 2 hr. of machining time by standard methods. Another application required 90 pieces per set. In producing 20,000 sets, a saving of 5,000,000 man-hours was established as compared with former methods. On some ideal parts, savings of 20 to 80 per cent in price may be achieved, frequently accompanied by many other advantages.

A "natural" for powder metallurgy, and one difficult to machine by normal methods, is a flange unit having the bore eccentric with the barrel. A far more difficult part in this respect is a cylinder of which the bore is irregular. This might be a blind hole, a bore with steps of different diameters, a pocket-like relief either single or multiple in number. Similarly, a depression in a part (like the cavity in an Allen headless screw) is easy for our process, but otherwise difficult. There is no machine-tool equipment designed and built for performing such operations on a production basis; consequently the savings are enormous.

LIMITATIONS

Limitations are both general and specific in nature. As a general example, sharp corners at points of intersection are detrimental. There must be a fillet of modest dimensions. Again, too large a fillet—that is, one of large or disproportionate dimensions—causes difficulty. Generally speaking, a chamfer on the outside diameter and inside diameter of a cylinder is preferred to a radius. Long barrels with thin sections should be avoided. An intricate flange-type unit should be of normal proportions as compared with a very thin flange, for example.

Reliefs, undercuts, etc., on either the inside diameter or outside diameter of the barrel are beyond the capabilities of present-day briquetting presses. We have studied designs of equipment for this provision, but the economics are still unfavorable.

This viewpoint, however, should be weighed: Suppose that you cannot finish the entire part by powder metallurgy; is it possible to do 70 or 90 per cent of the job to a very great advantage? As we know, the majority of parts produced by any manufacturer involve numerous operations on different machine tools; therefore, there are advantages in making a machine part from powdered metals, and arranging to perform subsequently the remaining finishing operations. Generally, these are the simplest types of machining operations.

Many things about the fabrication of parts from metal powders are not indicated on the operation sheet, which may read as follows: Mixing of the powders, compressing in an automatic briquetting punch press, heat-treating by sintering, oil impregnating, finishing to size in a punch press, recoil impregnating, and inspecting.

The dies are made from the best grade of tool steel, hardened, ground and lapped to approximately plug and ring gauge tolerances. A special technique applies to proper die design.

As yet we cannot set up a briquetting press as we do a milling machine or gear cutter, for a set block cannot be used. Each setup is different. However, improvement is being made.

We are among those who do not recognize size as a necessary limitation for powder metallurgy. Rather, we look at it from the standpoint of the economics involved. If the design is sound, the volume assured, and the economics favorable, we can probably undertake to make such a part, whatever its size.

Specifically, we are in production on parts 18 in. in diameter and are prepared to produce units considerably larger, say of the order of 36 in. in diameter, again subject to favorable economics. We have made bronze plates 20 by 30 by 1 in. and have studied production of a bar 6 by 2½ in. by 13 ft. long. Recently, I was shown the blueprint of a part 96 in. long, and a bearing 22½ in. in diameter, on which we are quoting.

Acceptable quantities vary widely and depend upon the economics involved. The problem is really very simple. Quotations are given for price, tool cost and delivery. If these combined factors are favorable, the design is applicable for powder metallurgy, assuming of course that the physical properties are also satisfactory. However, we are daily furnishing parts and powder metallurgy bearing-bar stock where one unit only is required. The material is supplied as a cored or solid bar stock. We cover a wide range of sizes. Thus a design or research problem may be attacked promptly, the parts tested, redesigned, and approved in a matter of days or hours instead of waiting for production tools. There are also applications in what might be termed the scientific field, where the quantity involved is six pieces or less. However, in such cases the service or performance is far beyond that which is possible from any known solid material. These items are a military secret and of course may not be discussed.

Design engineers, product engineers and scientists may find a ready answer in powder metallurgy when blocked by limitations of other material.

During the war program, our services and contributions have often featured the breaking of production bottlenecks. Some examples are making micrometer frames from powdered metals; producing toolmakers' V-blocks with a Rockwell hardness of 62C; manufacturing a height-gauge-base from powdered iron, etc.

Attractive physical properties have been obtained, such as 166,000 lb. tensile strength on test bars. Parts of such high tensile strength are not as yet in production, but the groundwork has been laid.

For possible applications for powdered metals engineering specifications should be studied. Often a specification is based on the *material used* and not upon the *actual stress* incurred.

Many engineers are iron minded. Prior to the present conflict all of this material was imported from Europe. American courage, initiative, enterprise and ability quickly stepped into the picture, and today there is available a greater quantity of iron powder of vastly improved properties, as compared with the European powder.

It is a pleasure to compliment the manufacturers of this highly superior powdered iron.

Sometimes we are surprised at the results obtained in the laboratories—not only mechanical advantages, but many others, including superior electrical characteristics. A long step forward is the manufacture of cored and bar stock made from powdered metal, which involves no die expense. The user simply machines the desired part from these stock items, tests, incorporates indicated changes, then forwards blueprints and orders his requirements. The standard cored and bar stock thus provides for the utmost expedition in the engineering of new machine parts.

DISCUSSION

(*Roland P. Koehring presiding*)

QUESTION.—Mr. Langhammer, do you anticipate any bottleneck in the supply of iron powder?

A. J. LANGHAMMER.—That is rather asking a question of the wrong man. However, I will reply to the question from our point of view. There is a considerable amount of iron powder available but the properties vary over a wide range. Powder metallurgy has progressed to the stage where we recognize certain requirements in powdered iron, and what may be a good powdered iron for one application will not necessarily fit the picture for the next one. Further, I believe that there is room for great improvement in the properties of powdered iron. Also, that there is only a limited quantity of powdered iron available having certain specific properties in which we are at the moment interested.

F. P. PETERS.—May I have a word? With all possible respect to the contributions of the Chrysler Corporation (and they have been tremendous) to the war effort, I think it is easy to get from part of Mr. Langhammer's discussion a false impression of vaster possibilities than really exist. It would be well if in addition to Mr. Langhammer some other manufacturers of machine parts might tell us in the next few minutes some of the limitations they have found. For example, what is the maximum tensile strength that is being produced in a commercial part in production today? And what is the actual size limitation on bearings that are in operation and are standing up well?

We should always bear in mind the fact—and I think Mr. Langhammer will agree with me—that quoting on a particular part does not necessarily mean placing it in production. In many cases it may be several months before the quotation is resolved and we know whether the part can be made. Let us open up this thing for a little free-for-all discussion of some of the ceilings that do exist in the design of machine parts made by powder metallurgy. The ceiling is not unlimited, and Mr. Langhammer will agree with that, I am sure.

H. HENDRIKS.*—I do not think that there is so much limitation in the making of powder metallurgic manufactured parts as mentioned. Last year we had the problem of making dies for a special machine used in the manufacturing of slide fasteners. This part was wearing out very fast. It was very hard to make, it had to be hobbed out of a special steel and it was a difficult thing to manufacture in general. The tolerances were one half of one thousandth of one inch on all dimensions. We submitted this die to a manufacturer of powder-metal parts. He thought that it was impossible, but we were not as skeptical as he was and decided to try it anyway.

The Canadian General Electric Carboloy Division, in Toronto, gave us then the design for the dies, which we made to their specifications. When the first part was delivered, we submitted it to our Inspection Department and its check showed that all the tolerances were right on the dot. They delivered 19 parts of exact specification, then they went off the beam; they could not keep to the tolerances. It took them a long time to get back again. We do not know what happened, but the main point I want to make is that if a problem is attacked in the right way, the dies are made right and corrected as to dimensions found out by experiment, I do not think that there is so much difficulty in making powder-metal parts to close tolerances.

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* Lightning Fastener Co. Limited, St. Catharines, Ont., Canada.

Intricate dies to be used in die-casting machines, which have to be made invariable by the hobbing method, restricting the use of some grades of tool steel and for such reason made out of softer grades of steel, will pit. Die-casting dies made out of tungsten carbide will outlast any made out of tool steel and in long run will pay more than the cost and effort to produce them.

Pole Pieces for Electric Motors Made from Iron Powder

By F. V. Lenel,* Member A.I.M.E.

This discussion is concerned with the method of manufacturing, the design possibilities, and the properties of pole pieces for direct-current electric motors and generators made from iron powder. In such applications as pole pieces, the electric and magnetic properties of the material are of major importance, therefore they are discussed somewhat more fully. However, the main advantage in making pole pieces from powders lies in the rapid and inexpensive method of manufacturing these pieces, and in the flexibility of design, rather than in their superior electrical properties. As a matter of fact, pole pieces from iron powder have found their principal field of usefulness in small electric motors for controls and similar applications where the highest possible flux density in a given design is not required.

Fig. 1 shows a number of different designs for pole pieces made from iron powder. The steps involved in fabricating them are: (1) briquetting—with each stroke of the briquetting press a complete pole piece is produced; (2) sintering, and (3) sizing, which is a one-step coining operation in a hand-operated punch press.

Conventionally small pole pieces are made from laminated electrical sheet steel stock by punching out the laminations and riveting them together (Fig. 2). The powder method has the advantage of being rapid and inexpensive; also, it makes possible the molding of pole pieces with a round hub, which are better from a design standpoint, as will be shown later. It is difficult to make such round-hubbed pieces from laminated stock. The pole pieces could, of course, be machined from solid stock, but this method is not widely used.

The raw material for making pole pieces from powder is straight iron powder without the addition of any alloying ingredients. However, the grade of powder used is of considerable importance, as will be shown later when the influence of the grade of iron powder upon the magnetic properties is discussed.

Pole pieces are briquetted in the same way that other iron-powder machine parts are made. Because the pole pieces are flanged—i.e., they have a hub and a wing section—they are made in presses that apply pressure from both ends. For best mechanical and magnetic properties, the density throughout the piece should be even and also should be constant from piece to piece. For that reason a powder of constant compressibility from batch to batch is needed for briquetting pole pieces.

One method of obtaining the required magnetic properties is to sinter the pole pieces at temperatures higher than are used for most iron-powder parts. A temperature of 2400°F. and an atmosphere of hydrogen has been found satisfactory. No automatic furnaces of the roller hearth or mesh-belt type have yet been developed for such high temperatures. A box-type furnace heated with Globar heating ele-

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* Moraine Products Division, General Motors Corporation, Dayton, Ohio.

ments having an attached cooling zone is therefore used. The pieces are sintered for 1½ to 3 hr., depending on the size of the pieces and the magnetic properties required.

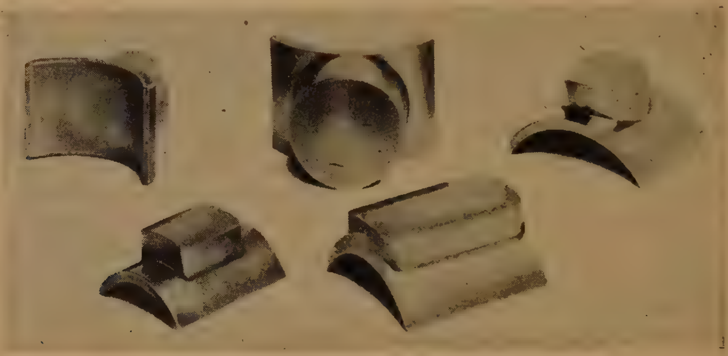

FIG. 1.—POLE PIECES MADE FROM IRON POWDER.

The sintered pieces are ready for sizing, which is the conventional coining operation used to bring the pole pieces to final size.

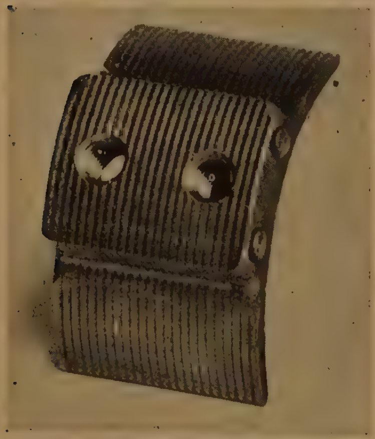

FIG. 2.—POLE PIECE MADE FROM LAMINATED ELECTRICAL SHEET STEEL.

The principal magnetic property that determines the performance of pole pieces in direct-current electric motors is their magnetic permeability. The permeability is the ratio of the flux density (in lines per square inch) induced in a material to the magnetizing force (in ampere turns per inch) that is applied to it. The flux density in the various parts of the magnetic circuit and the dimensions of the circuit determine the magnetic flux, which is one of the prime design data of a d.c. electric motor, upon which both the torque and the speed of the motor depend. This flux should be obtained with a small number of field ampere turns; or, in other words, the permeability of the various components of the magnetic circuit should be high, for two reasons: (1) the smaller the number of turns, the less space is required for the winding, (2) the smaller the number, the less power will be lost through resistance losses in the winding and the higher will be the efficiency. However, the permeability of one of the components of the magnetic circuit—the air gap—is fixed because the permeability of air is one by definition. Because of this low permeability, the design of the air gap will greatly influence the electrical characteristics of the motor. On the other hand, the permeability of the pole-piece material should be high, and, even more important, it should be the same from piece to piece, otherwise it would be necessary to have a different number of turns for each motor, which, of course, is impractical.

Fig. 3 shows the curves of flux density versus magnetizing force and in the same diagram the curves for permeability versus flux density for a material made from powder and for electrical sheet steel. Both metric and English units are given. As is well known, flux density and magnetizing force in ferromagnetic materials are by no means proportional. At low values the flux density rises very rapidly with increasing magnetizing force, while at higher values the flux density increases less and less rapidly, until finally saturation is reached and the induction does not increase any more with rising magnetizing forces. Therefore, the permeability is not a constant, but goes through a maximum and then declines again. The flux density in the pole piece upon which the design of the small d.c. electric motors is based may be assumed to be in the neighborhood of 55,000 to 65,000 lines per square inch. This flux density can be obtained with fewer ampere turns per inch in an electrical sheet-steel pole piece than in the iron-powder pole piece, and it is therefore necessary to put some extra turns into the field coil to compensate for the lower permeability at this flux density, when a steel pole piece is replaced by an iron-powder pole piece. The difference is not as great as might be inferred from the values on the curve because, as indicated above, the total number of turns necessary to establish the field in the pole pieces is small compared with the number of turns necessary to bridge the air gap with magnetic flux, possibly only 10 per cent. Besides, there is a compensating feature in the design flexibility of iron-powder pole pieces. The round hub of these pole pieces accom-

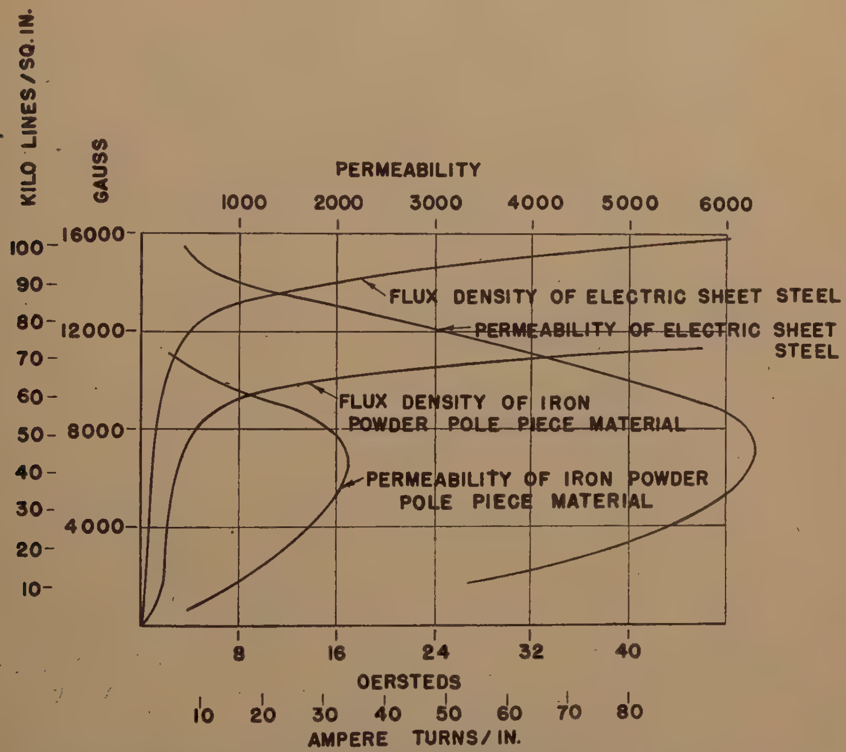

FIG. 3.—MAGNETIZATION AND PERMEABILITY OF MAGNETIC MATERIAL MADE FROM POWDER AND OF ELECTRICAL SHEET STEEL.

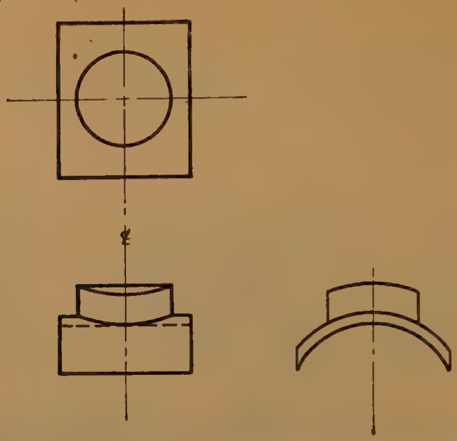

FIG. 4.—DESIGN OF POLE PIECE MADE OF IRON POWDER.

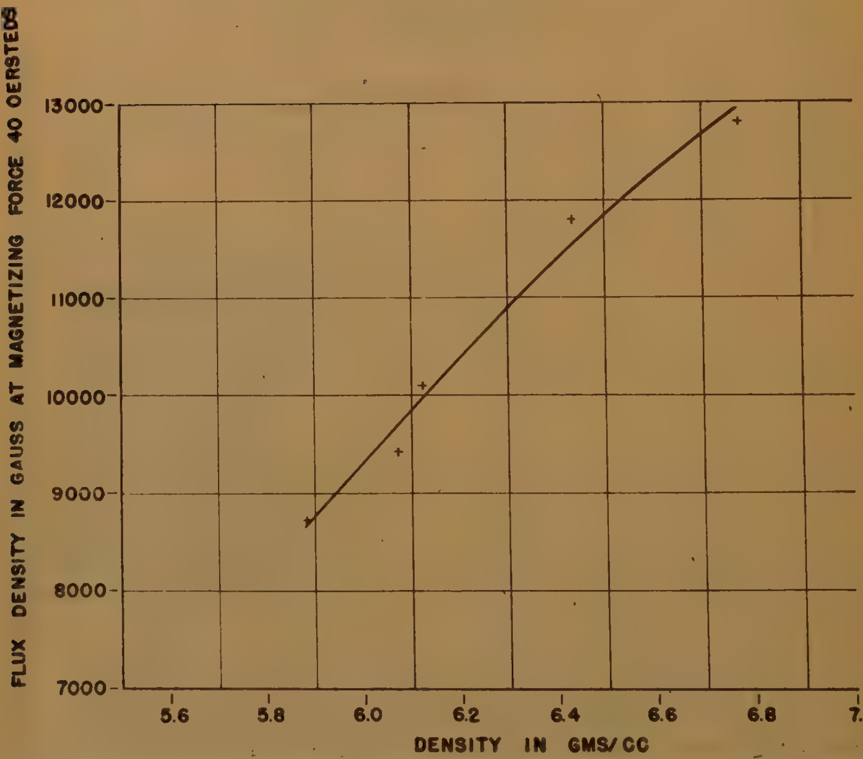

FIG 5.—RELATION BETWEEN SINTERED DENSITY AND FLUX DENSITY AT A MAGNETIZING FORCE OF 40 OERSTEDS.

modates a round coil. The forms for such a round coil are easier to wind than those for a rectangular coil. They also require less copper wire per turn. This saving in copper wire will go quite a way to make up for the extra turns which are necessary to compensate for the lower permeability of the iron-powder pole piece. Furthermore, there are advantages in a design like that shown in Fig. 4, where the hub does not extend all the way to the edge of the wings. More room is provided for placing the field coil turns and it may even be possible to make the pole piece shorter than in the conventional design.

Hysteresis and eddy-current losses, which are very significant in alternating-current applications, are of minor impor-

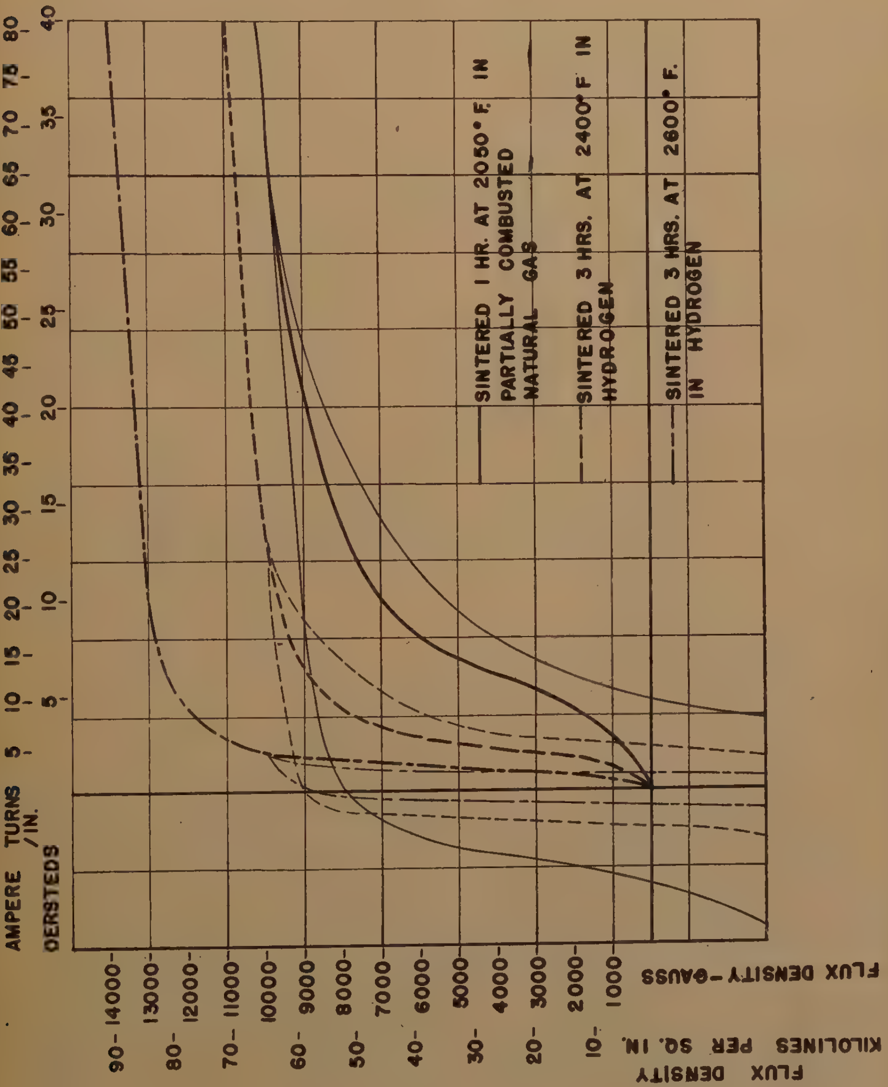

FIG. 6.—EFFECT OF HEAT-TREATMENT UPON MAGNETIZATION CURVE AND HYSTERESIS LOOP OF MAGNETIC MATERIAL MADE FROM IRON POWDER.

tance in pole pieces for d.c. electric motors, because the electric current through the field coils of the motor is constant. Therefore, the magnetic field emanating from the pole pieces of a d.c. motor is constant except for small fluctuations, which are caused by the fact that the surface of the armature has teeth and slots. When these teeth and slots move underneath the pole piece, they induce small fluctuations in the field and thereby cause very small hysteresis and eddy-current losses. These small losses are negligible in the small motors that are under discussion but have to be considered in large d.c. motors and generators where even the smallest gains in efficiency cannot be overlooked. The hysteresis losses in a given magnetic material depend on the composition, heat-treatment, mechanical stresses, etc. The eddy-current losses may be reduced to a small percentage by increasing the electrical resistance along the path of the eddy current. This is usually achieved by using sheet-steel laminations insulated from each other, instead of solid material. Pole pieces with laminated shoes are required, therefore, in large direct-current machines.

TABLE 1.—*Magnetic Properties of Ring Samples*

Briquetted at 60,000 lb. per sq. in. sintered 3 hr. at 2400°F. in hydrogen

Source of Iron Powder	Radial Shrinkage of Samples in Sintering, In. per In.	Density of Sintered Sample, Grams per C.C.	Max. Permeability	Magnetizing Force, Oersteds for Flux Density of 10,000 Gauss	Flux Density, Gauss for Magnetizing Force of 40 Oersteds	Residual Induction, Gauss from 10,000 Gauss	Coercive Force, Oersteds from 10,000 Gauss
Electrolytic	0.008	6.82	3100	3.9	12,700	9300	1.6
Decarburized comminuted steel shot	0.012	6.69	2150	14	11,000	9000	2.0
Hydrogen-reduced mill scale	0.018	6.20	1340	30	10,300	8500	3.1
Hydrogen-reduced oxide from steel scrap	0.023	6.01	1380	40	10,000	8300	2.9

A magnetic material as described in this paper for pole pieces is suitable only for applications where a constant magnetic field is involved. Because of the high eddy-current losses in the material, it should not be considered where the magnetic field alternates between positive and negative values as in all a.c. machines and also in the armatures of rotating d.c. machines. The electrical resistivity of the material, which largely controls eddy-current losses, is only 1½ to 3 times that of pure iron and compares even less favorably with the resistivity of silicon steel. In all such applications it is necessary to use a laminated and not a solid material.

Table 1 and Figs. 5 and 6 illustrate how the magnetic properties of pole pieces are influenced by the choice of raw material, the density to which they are briquetted and the heat-treatment they receive. These diagrams emphasize the necessity of control so that at all times pole pieces of the same permeability are supplied to the manufacturer of electric motors.

Table 1 gives the magnetic data on samples made from a number of different iron powders. All samples were briquetted at a pressure of 60,000 lb. per sq. in. and sintered 3 hr. in hydrogen at a temperature of 2400°F. Powder made from electrolytic iron is a very satisfactory material, having a high flux density; next in line comes iron powder from decarburized, comminuted steel shot, which has been used satisfactorily for pole pieces. Iron powders made by reduction are less suitable.

Fig. 5 shows the relationship between sintered density and flux density for a number of samples. As is expected, the flux density increases with increasing sintered density. This is the reason why the density must be controlled in the manufacturing process, so that the permeability is kept constant.

Fig. 6 shows the magnetic induction curves and hysteresis loops for samples briquetted with 30 tons per sq. in. from decarburized comminuted steel shot and sintered in three different ways. Curve 1 refers to a sample sintered 1 hr. at 2050°F. in partially combusted natural gas; curve 2 refers to a sample sintered 3 hr. at 2400°F. in hydrogen; curve 3 to a sample sintered 3 hr. at 2600°F. in hydrogen. Higher temperatures and longer sintering times greatly increase the permeability and decrease the hysteresis losses in material made from iron powder. The last sample shows magnetic properties almost equivalent to electric sheet steel, but such a high-temperature treatment would be expensive because of the low capacity of the necessary furnace equipment. The treatment at 2400°F. has given pole pieces that were acceptable for the application.

DISCUSSION

(Roland P. Koehring presiding)

R. P. Seelig.*—Dr. Lenel is to be congratulated on his presentation of a particularly interesting paper describing the use of the powder metallurgy process for the production of magnetic pole pieces.

The only thing that might be added is that we have been successful in producing pole pieces with a narrow hysteresis curve by the use of considerably lower sintering temperatures than the ones used by Dr. Lenel. It is quite possible that this use of lower temperatures has considerably widened the field of commercial application for pole pieces made from metal powders.

Development work is currently being done on an a.c. application of a sintered iron part. However, I am in full agreement with Dr. Lenel that if eddy currents are an important factor in the application, we cannot substitute sintered material for laminated sheet-metal structures.

Mr. Peters' remarks concerning the limitations of machine parts were well taken. The emphasis of the limitations makes it easier to define clearly what we can do and what the advantages are of machine parts made of metal powders.

When I mention metal-powder machine parts, I mean those of relatively high density, although complete elimination of porosity is not possible at this time. The limitations of the field for this type of parts are largely economical. I believe that Mr. Langhammer has made that point very clear. The following questions are very often asked: How large a part can you make? How close can you hold the dimensions? How fast can a part be produced? In a majority of the cases, it depends on the cost at which the part can be produced. A large variety of shapes and sizes of a number of materials can be formed. However, the main requirement in this field of endeavor is whether this can be done more economically by powder metallurgy than by other manufacturing methods.

As a general indication, it may be stated that densities up to 95 per cent of that of rolled material can now be produced commercially in simpler parts. Tolerances of plus or minus 0.001 in. are common, but where special conditions justify, closer tolerances can be held; we are producing a part of which one dimension is held to 0.0003 inch. Finally, as far as maximum size is concerned, technically this would depend on the capacity of the press and furnace equipment available. Actually, we find that the economical limit of powder-metallurgy machine parts is approximately one pound. From there on, each individual case must be studied on its own merits.

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* Powder Metallurgy Corporation, Long Island City, N. Y.

Bearings from Metal Powders

By W. R. Toeplitz,* Member A.I.M.E.

Probably a more descriptive title would be "Much Ado About Nothing." By "nothing," of course, I refer to the porosity which is the main feature of this type of bearing. Porosity has a decided effect on the manufacturing techniques, the structure and physical properties, the oil content, and on the installation and service of oil-retaining porous bronze bearings.

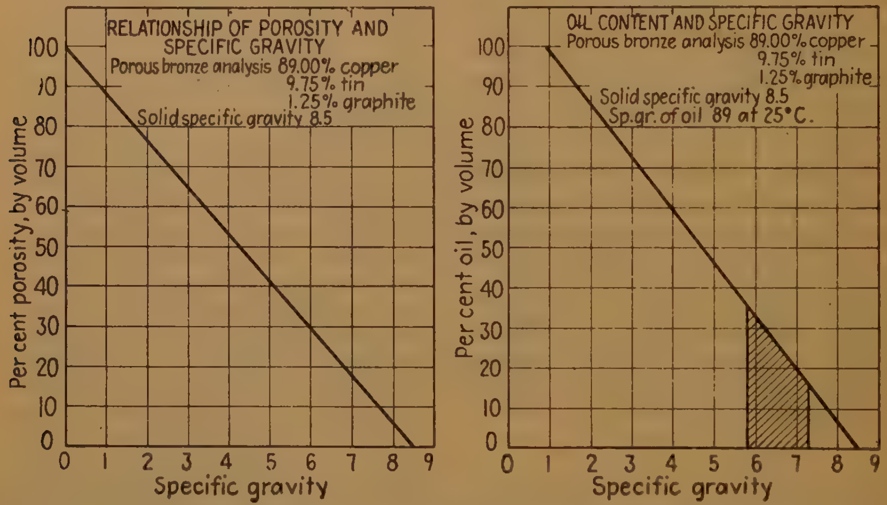

Fig. 1.—Relationship of (*a*) porosity and specific gravity and (*b*) oil content and specific gravity.

A simple curve can be drawn by plotting specific gravity along the abscissa and percentage of porosity by volume on the ordinate. A bronze composition, analyzing 89 per cent copper, 9.75 per cent tin, and 1.25 per cent graphite, has an absolute solid specific gravity of 8.5. At this specific gravity, of course, occurs the point of zero porosity. Conversely, at 100 per cent porosity, the specific gravity is zero.

A similar curve can be drawn for bearings impregnated with oil; the only change being that the specific gravity at 100 per cent oil will be 0.89 if we assume that that is the specific gravity of the lubricant. The curve is useful in determining the oil content by volume for any specific gravity.

The normal range of oil content for porous bronze bearings of this composition is from 35 to 16 per cent, which is in the specific gravity range of from 5.8 to 7.3.

In addition to the amount of porosity, the type of porosity is important. The first consideration here is that the porosity must be intercommunicating. This can be determined by a number of simple tests.

The first method, which is very accurate, is to extract the oil in the bearing by cycling

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Manuscript received at the office of the Institute March 8, 1944.

* Metallurgical Engineer, Bound Brook Oil-Less Bearing Co., Bound Brook, New Jersey.

in the soxhlet with a solvent followed by drying, then reimpregnating the bearing in a vacuum and determining the percentage of oil by volume by computation. This, together with the specific gravity, may be compared with the theoretical curve and reasonably close correlation, within 3 per cent, is proof that the porosity is of the intercommunicating type. There are many simpler ways of determining this; for example, heating the bearing should cause oil sweat on all surfaces or a liquid may be forced through the wall by light pressure such as may be applied with the fingers, a plug gauge, or a fixture actuated by a rubber bulb.

To arrive at the size of the pores is difficult. Several years ago we made a series of tests on a large bearing having 21 sq. in. of porous surface in the bore. Liquid was forced through the wall of this bearing under a static head. We then made a series of small orifices to determine what the total flow through this large area amounted to in terms of a measureable orifice. We found that this was equivalent to an orifice 0.007 in. in diameter. Since the volume of this bearing was 4.46 cu. in. and it contained 25 per cent porosity by volume, if all of this porosity were gathered in a single hole it would be 1.49 in. in diameter through the 3⁄16-in. wall of the bearing. These figures serve only to indicate that the pores are truly capillary in size and that the flow of a liquid through a porous structure is no index of the total number of pores supporting the oil film, as thousands are so small they will pass only a negligible amount of oil in a short time under pressure but are invaluable in supporting the oil film and feeding extremely small amounts of oil by capillary attraction in service.

Regarding the effect of porosity on the structure and the resulting physical properties of porous bearings, Fig. 2 indicates the variation of physical properties with specific gravity. As is to be expctted, the physical properties improve as the oil content decreases.

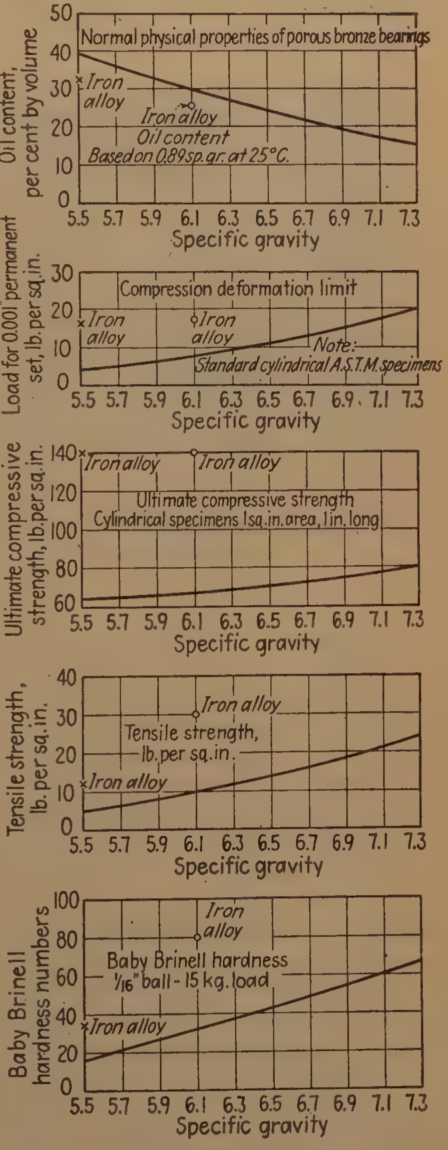
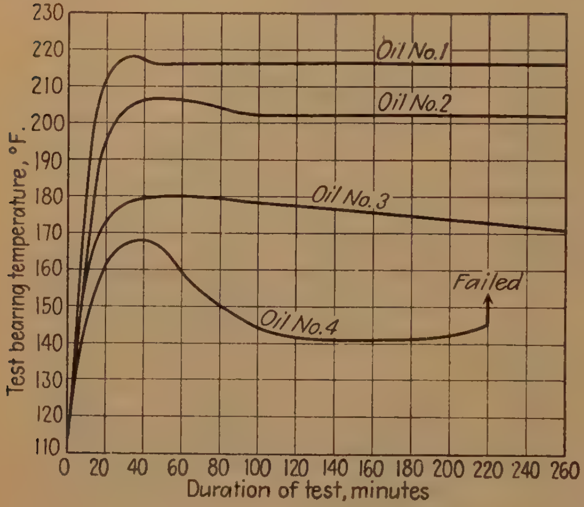


FIG. 2.—EFFECT OF POROSITY ON STRUCTURE AND PHYSICAL PROPERTIES OF POROUS BEARINGS.

In selecting a bearing for an application, it is necessary to consider both the oil content and the strength. A bearing for a

½-in. shaft with a $\frac{1}{16}$-in. wall an inch long, and containing 25 per cent oil by volume, actually contains only 10 drops of oil. If no additional oil is supplied, these 10 drops must (and are able to) lubricate the bearing for life. It is advisable to use, for average applications, bearings within a specific gravity range of from 6.2 to 6.8. This is based on years of experience with many thousands of satisfactory installations. Regarding loads and speeds, porous bronze in this specific gravity range may be used as a bushing, with no rotation, at a load of 8000 lb. per sq. in. projected area. For slow and intermittent service, 4000 lb. per sq. in. and with a shaft velocity of more than 200 ft. per minute, the formula $PV = 50{,}000$ may be used, in which P indicates the load per square inch of projected area and V the shaft velocity in feet per minute.



Viscosity, Saybolt

Oil No.	100° F.	150° F.	210° F.
1	1,650	576	152
2	660	237	81
3	102	59	40
4	53	41	33

Test Conditions

Bearing size, in.	1 × 1¼ × ¾
Shaft size, in.	0.998
Clearance, in.	0.0023
Speed, r.p.m.	2600
Total load, lb.	56.5
PV factor	51,250

Other Data

Shaft material, cold-rolled steel
Bearing composition: Cu, 89 per cent; Sn, 9.75; graphite, 1.25.
Oil content, 27 per cent by volume.

FIG. 3.—OPERATING TEMPERATURE VS. VISCOSITY OF LUBRICANT.

If higher strength is needed, the specific gravity may be increased, or if loads are extremely light and there is no additional means of providing a lubricant, making maximum oil content the main factor, the specific gravity may be reduced as low as 5.8. If it is necessary to get higher physical properties with the same oil content, it is possible to change to a different alloy. As indicated on Fig. 2, an iron-copper alloy containing 25 per cent of oil has greatly increased physical properties over a porous bronze bearing of the same oil content. Also, it is possible to use an iron-copper alloy of a lower specific gravity in order to secure a higher oil content while still maintaining the physical properties of a porous bronze bearing of lower porosity. A higher strength iron bearing will carry a load of 20,000 lb. per sq. in. projected area with no rotation, 7500 lb. per sq. in. at slow speeds, and at higher speeds a PV factor of 60,000 may be applied. Bronze is still the preferable alloy because of its antiseizing characteristics.

It is interesting to note that the hardness figures are very low. This is, of course, because in testing we are breaking down the porous network rather than measuring the hardness of the particles. The actual grain hardness is the same for the porous materials as it is for the cast type.

The porosity is also a measure of the oil content and, strangely, oil or other lubricant is perhaps the most important component of an oil-less bearing. This extremely small amount of oil distributed through the maze of capillary pores must efficiently lubricate the bearing for its entire service life unless some means of additional lubrication is supplied. The journal starts on an oil film and as the temperature rises, owing to friction, more oil is forced out of the pores, because the cubical coefficient of expansion of the oil is much greater than that of the metal. When rotation stops and the bearing cools down, the oil is reabsorbed by the capillary structure. Under these conditions the oxidation resistance or stability of the oil is extremely important.

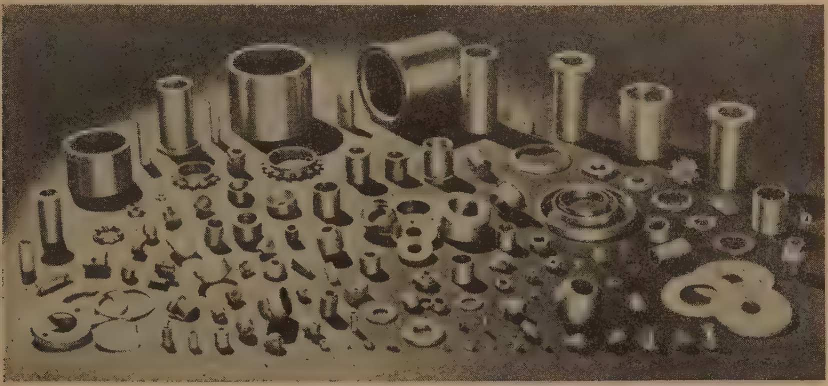


FIG. 4.—BEARING SHAPES.

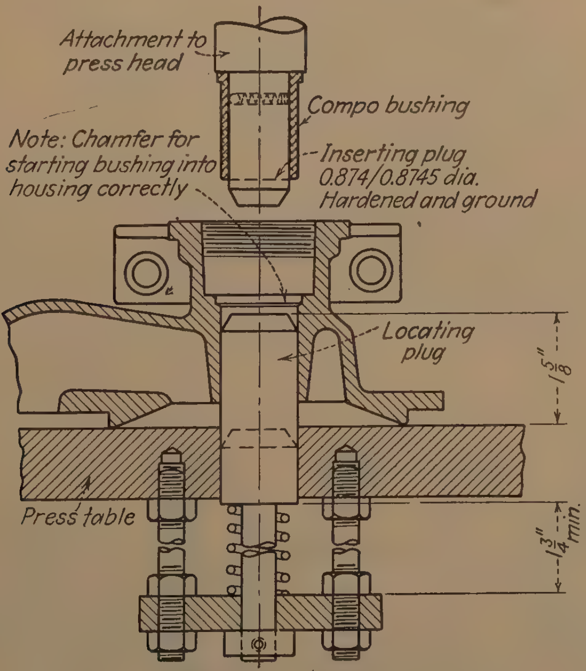

Attachment to press head
Compo bushing
Note: Chamfer for starting bushing into housing correctly
Inserting plug 0.874/0.8745 dia. Hardened and ground
Locating plug
1 5/8"
Press table
1 3/4" min.

FIG. 5.—STANDARD METHOD OF INSTALLING BEARINGS.

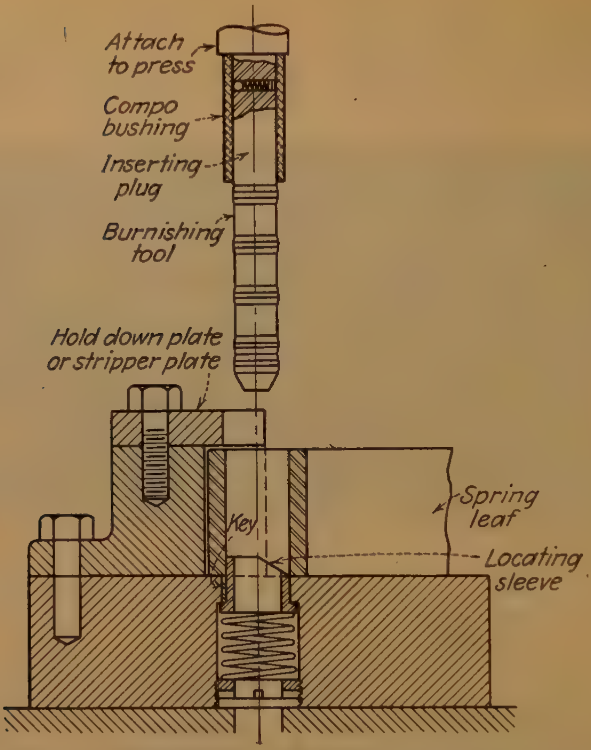


FIG. 6.—COMBINATION INSERTING AND BURNISHING TOOL.

Bushing bore as finished is larger than maximum diameter of burnishing tool.

Operator places bushing on inserting plug, then depresses locating sleeve with end of spring leaf and slips spring leaf into socket until locating sleeve springs up into position. On the downstroke the bushing is pressed into the spring eye, the bore closing in on the plug. On the upstroke the bore of the bushing is burnished to finish size. Spring leaf is then free to be withdrawn as locating sleeve is depressed below table by the bushing.

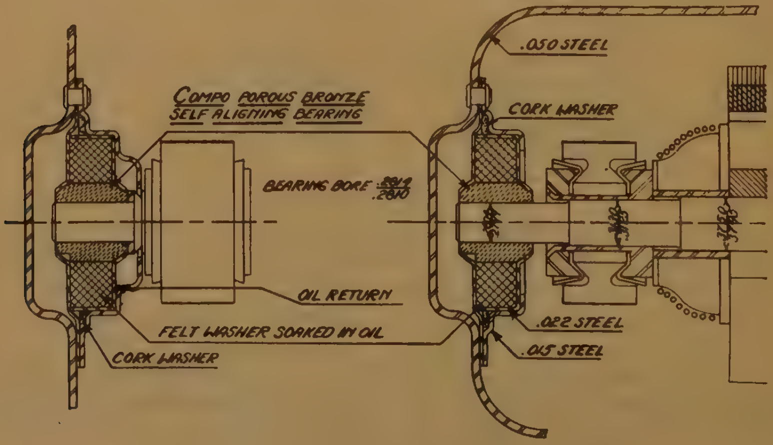

COMPO POROUS BRONZE SELF ALIGNING BEARING
BEARING BORE .2814 / .2810
OIL RETURN
FELT WASHER SOAKED IN OIL
CORK WASHER
.050 STEEL
CORK WASHER
.022 STEEL
.015 STEEL
.3750

FIG. 7.—SELF-ALIGNING BEARING INSTALLATIONS.

Most manufacturers have found it necessary to do considerable research work on oils, as the data submitted by oil companies on engine tests, etc., are not indicative of the conditions and results found in oil-less bearings. Oils are selected on the basis of their oxidation resistance, viscosity, and performance in a running test. Regarding the effect of viscosity, this is the same as in conventional bearings, and Fig. 3 indicates that the operating temperature is largely a function of the viscosity of the lubricant. However, it should be borne in mind that the load-carrying capacity of the bearings increases with increasing viscosity of the oil.

One of the features imparted by the porosity of these bearings is flexibility over a wide range of temperatures. Since oil-less bearings have only a very thin film for lubrication without any excess oil or grease, they are ideally suited for low-temperature applications. It is necessary only to use an oil that solidifies to a soft, paraffinic wax. This wax will act as a satisfactory lubricant until the bearing temperature rises to a point where the oil becomes fluid. In this way, it is possible to use oils of higher viscosity, which give better service at normal and elevated temperatures than the conventional types of extremely light oils or greases that must be used in ordinary bearings for low-temperature service.

Porosity is again a most important factor in the manufacturing of these bearings from metal powders. As an example, in the sintering of a compact where there is a constituent that melts, such as tin in bronze, this constituent is distributed throughout the structure by capillary porosity. The amount of porosity has a great effect on size changes of the compacts during sintering. Also, the porous structure enables the gases of the furnace atmosphere to penetrate through the compact and reduce oxide films, etc. The presence of considerable porosity also permits sizing to extremely close tolerances. For bearings up to 1½ in. in diameter, it is a standard practice to finish the bore and outside diameter within the total tolerance of 0.001 in. and the length to a total tolerance of 0.010 in. This is possible because the bearing may be sized in the bore, outside, and length in one press operation without a flash or appreciable burr, as it is compressible. This feature is extremely important. Fig. 4 shows a number of bearing shapes currently being produced.

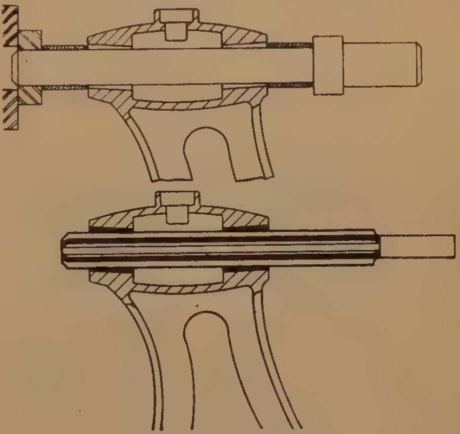
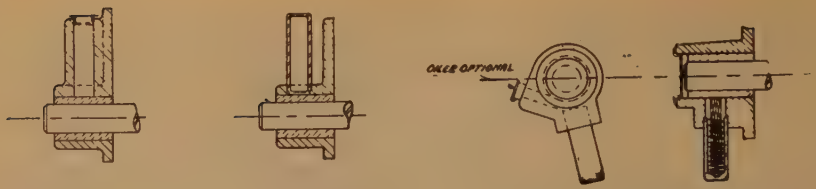


Fig. 8.—Two bearings being installed without align reaming by means of long plug.

The standard method of dimensioning bearings is to make them 0.003 to 0.004 in. larger on the outside diameter and inside diameter and insert them with a plug, as shown on Fig. 5. This plug is dimensioned in such a manner as to give the correct bore size, which probably is 0.0015 in. less than the original bore. This includes somewhat further compressing of the wall and perfect alignment of the bearing with a plug. In all cases, a smooth, mirror-finish surface is maintained. A button burnishing tool may be used to secure extremely close tolerances. Fig. 6 shows a combination inserting and burnishing tool. Spherical self-aligning bearings may be installed in light sheet-metal housings, leaving them free to align themselves with the shaft as shown in Fig. 7.

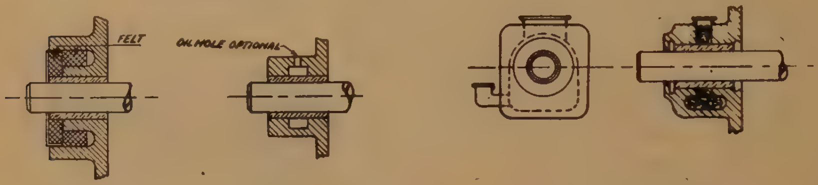


Reservoir cast in housing

Steel-shell reservoir

Gravity feed

Wick feed



Wool-felt saturated with oil

Groove in housing

Cored recess packed with oil-soaked waste

FIG. 9.—COMMON METHODS FOR PROVIDING ADDITIONAL OIL.

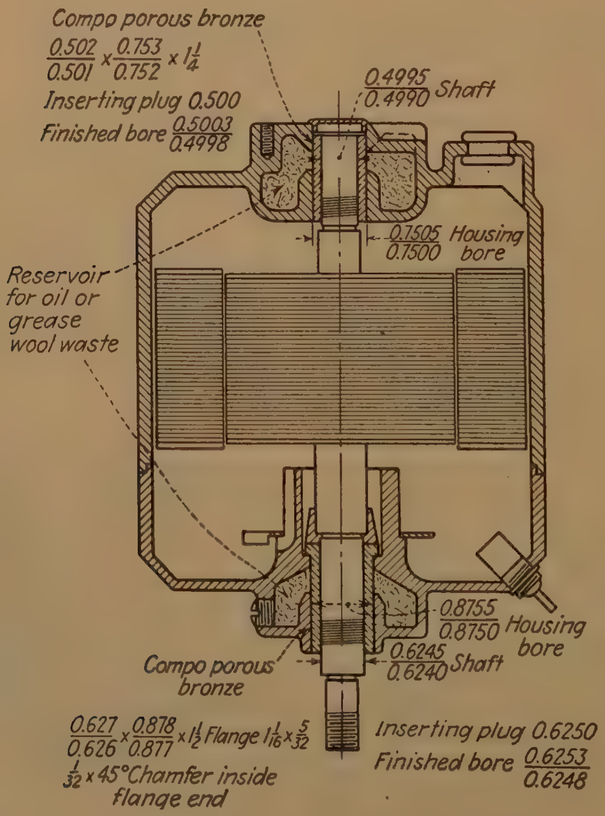

Compo porous bronze
$\frac{0.502}{0.501} \times \frac{0.753}{0.752} \times 1\frac{1}{4}$
Inserting plug 0.500
Finished bore $\frac{0.5003}{0.4998}$
$\frac{0.4995}{0.4990}$ Shaft
$\frac{0.7505}{0.7500}$ Housing bore
Reservoir for oil or grease wool waste
$\frac{0.8755}{0.8750}$ Housing bore
$\frac{0.6245}{0.6240}$ Shaft
Compo porous bronze
$\frac{0.627}{0.626} \times \frac{0.878}{0.877} \times 1\frac{1}{2}$ Flange $1\frac{1}{16} \times \frac{5}{32}$
$\frac{1}{32} \times 45°$ Chamfer inside flange end
Inserting plug 0.6250
Finished bore $\frac{0.6253}{0.6248}$

FIG. 10.—TYPICAL OIL-LESS BEARING INSTALLED IN VERTICAL FAN.

Fig. 8 shows two bearings being installed without align reaming by means of a long plug. Compressibility of the parts owing to their internal porosity permits extremely good alignment; using an align reamer is not nearly as satisfactory, because the shaft tends to run on several lands that originally were high spots.

Fig. 9 shows some of the common methods for providing additional oil. The oil is fed directly through the wall of the bearing and filtered in the process. Oil holes and grooves are completely eliminated.

Fig. 10 shows a typical oil-less bearing installed in a vertical fan. It shows a plain pipe bearing and a flange bearing to take the thrust from the collar on the shaft. Additional oil has been provided by means of cored holes in the fan housing filled with wool waste and the shaft has grooves for returning the oil.

Metallurgically speaking, "porosity" is an ugly word. However, in the case of oil-less bearings, controlled porosity makes it possible for the metallurgist to combine in a single structure both a bearing alloy and its lubricants. This is truly functional design.

DISCUSSION

(*Roland P. Koehring presiding*)

H. N. GHENN.*—It has been established that the accuracy obtainable from any precision machine is a function of the wear resistance, maintenance and closeness of fit of the bearings, hence I would like to ask Mr. Toeplitz how these oil-less bearings compare with cast iron or babbitt or similar materials when used on precision machinery. Could these bearings be used, for example, on a grinding machine in which work must be held to a tolerance of plus or minus 0.000025 inch?

W. R. TOEPLITZ.—The metal-powder bearings can be held to very close tolerances and are used in place of cast iron and babbitt on precision machinery.

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* American Viscose Corporation, Marcus Hook, Pennsylvania.

Brushes and Allied Powder-metal Parts

By R. R. Hoffman*

The name "brush," as applied to the parts to be briefly considered in this paper, is not clearly descriptive of the design and function of those parts when the usual definition of the word is applied. In a general way, the brushes to be considered here are the parts employed on certain types of electrical equipment to facilitate the transfer of electrical current between a rotating or moving element and a stationary element. These machines are generally motors and generators of both the slip-ring and commutator types, rotary converters, battery charges, etc. Parts that serve a similar purpose on relatively slow or intermittently moving devices such as rheostats, switches, controllers, etc., are generally referred to as contacts. A few special applications involve the use of current-carrying washers, rollers, bushings, etc.

As may be inferred, therefore, the design of these brushes and allied parts is dictated by both electrical and mechanical considerations. In most cases these factors are closely interrelated, and unfortunately many of them are not subject to exact scientific or mathematical analysis.

Special Advantages

Since brushes operating on direct-current machines must carry the load current, resist destructive action from voltage induced in imperfectly compensated armature coils, and in addition act as a bearing material, maintaining intimate contact with the commutator at peripheral speed, which may be as high as 70 miles per hour it is difficult to obtain in one brush the ideal properties necessary for perfect functioning under all operating conditions. The engineer-designer, therefore, when selecting a brush for a specific application, must choose a grade that possesses the characteristics most adequate to meet the conditions involved. In many cases a characteristic that makes a specific grade of brush the ideal selection for one type of machine may be of secondary importance to some other property when the brush is applied on another machine. Frequently different grades of brushes must be applied to the same type of machines when they operate under different or unusual atmospheric conditions.

Completely satisfactory brush operation depends on freedom from appreciable sparking, minimum electrical and mechanical losses, negligible commutator or slip-ring wear, uniform film over the commutator or slip ring, quiet operation and good brush life.

The ability to produce special structures, and to combine in widely varying proportions materials that are incompatible, through conventional melting and alloying procedures has been the basic contribution of powder metallurgy to the solution of problems involving brushes and allied parts. This is especially true where current-carrying capacity is a major factor, owing to the limitations of all carbon or all graphite brushes in that respect.

Metal-graphite Brushes

With very few exceptions, friction between moving elements, across which

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* Director of Research, Keystone Carbon Co., St. Mary's, Pennsylvania.

current must flow, cannot be reduced by conventional lubricants such as oils or greases, because their insulating characteristics and decomposition under electrical influences interfere seriously with current flow, introduce severe electrical losses and result in erratic performance. Because of its antifrictional properties, electrical conductivity and stability, graphite is very helpful in building up and maintaining, between such moving elements, a stable film, which is satisfactory as to friction, contact drop and minimum wear. On the other hand, certain metals, particularly copper, although high in frictional properties, are desirable because of their high electrical and thermal conductivities.

By combining these two basic materials, graphite and metals, in the form of powders, which produces a fine-grained, uniform structure, it is possible to secure the best compromise between all of the requirements for satisfactory brush operation on low-voltage, high-current machines. To what extent the use of metals in brushes raises the current-carrying capacity may be illustrated by the fact that plain carbon grades will carry between 35 and 50 amp. per sq. in. while the highest content graphite grades will carry only about 70 amp. per sq. in. continuously. High metal grades are rated at 125 to 150 amp. per sq. in., but will carry 450 to 500 amp. per sq. in. momentarily without undue heating.

It should not be inferred from this that the use of metal powders in brushes is the answer to all brush problems. On the higher-voltage, lower-current machines, all carbon and all graphite brushes, with their higher resistivities and higher contact drops, give performance that could not be duplicated by metal grades. As mentioned before, no one type or grade of brush combines all of the characteristics necessary for good performance on all of the widely varying kinds of applications.

There are two types of metal-graphite brushes. In one the metallic powders are held together by means of a bonding agent such as pitch or tar. These generally contain the lower percentages of metallic powders and the bonding material is required because there is not sufficient continuity of metal to provide the required strength by sintering or alloying. The other type, containing the higher percentages of metal, requires no bonding agent, the actual sintering of the metal particles giving sufficient strength.

The chief metallic constituent of almost all metal-graphite brushes is copper, but in many cases smaller amounts of tin, zinc, lead, etc., are added to promote bonding through an alloying action or to impart certain desirable characteristics to the brushes. Lately, silver-graphite brushes have come into considerable prominence because of superior performance in certain application, despite their higher cost.

An interesting sidelight on the possibilities of powder metallurgy is presented by the fact that when flake powders are used in forming the brush a laminated structure results, and if the molding pressure is applied at right angles to the direction in which current is to flow the electrical resistance will be lower in the direction of current flow than at right angles to it. This is of some value in operation of brushes on commutator-type machines.

DESIGN OF BRUSHES AND PARTS

The physical design and shape of brushes and allied parts varies widely, ranging from simple blocks of material to complicated shapes involving bevels, shoulders, slots, grooves, concaves, recesses, etc. Often this is further complicated by the necessity of attaching flexible shunts to ensure low resistance between brush and holder, the addition of lifting clips, etc. These variations in design are dictated by the individual requirements of the various types of equipment on which they are used.

Consequently, except for relatively simple high-production items, such as automotive starter and generator and small motor brushes, and for simple current-carrying washers, rollers, etc., it has not been found practical or economical to mold these parts to the exact size and shape desired. For some purposes they are molded approximately to shape and size, with only minor finishing operations; for others, the material is molded into the shape of blocks, from which a number of parts may be cut. In both methods, the finished size and shape is arrived at by conventional machining and grinding operations. Therefore there are few limitations as to shape or complexity of design except the cost of performing these finishing operations. Shunts are attached by bolting or riveting or are tamped in with special materials. Sometimes it is possible to mold in the shunt during the pressing operation. Clips are attached by bolting or riveting.

From a manufacturing standpoint, there are no serious limitations as to size. Obviously, by grinding or machining, parts can be made as small as the strength and structure of the material will permit. Large sizes would be limited only by the capacity of presses, and nonuniform density resulting from die friction, which is minimized by the large amounts of graphite present. Actually, size limitations imposed by operating requirements have prevented these manufacturing limitations from being approached.

Because increase in size means increase in weight and inertia, a number of smaller brushes operate more satisfactorily than a very large brush, maintaining uninterrupted contact with the moving element by more readily following slight irregularities and eccentricities. They also are more effective in dissipating the heat developed by electrical and mechanical losses. To give some idea of standard practice, the largest brushes are of the order of 1½ in. thick by 2 in. wide by 3½ in. long. The smallest are ¼ in. long, ¼ in. wide and ⅛ in. thick.

TOLERANCES

Likewise, because final dimensions, which are important, are arrived at generally by grinding or machining operations, permissible tolerances are not directly related to control of variables in the molding and sintering processes. Standard practice is a compromise between tolerances required for satisfactory installation and operation and cost of performing these finishing operations to varying degrees of precision. The more important dimensions are the width and thickness, as these determine the fit in the brush holder or other supporting mechanism. This clearance must be sufficient to permit free movement of the brush lengthwise in the holder, so that it can follow slight irregularities on the moving surface and so that the pressure mechanism can transmit pressure to the brush face without hindrance, and take up reduction in length due to wear. Consideration must be given also to the relative thermal expansions of brushes and box-type holders. Excessive clearance is undesirable because of undue lateral movement of the brush in the holder and uneven wear, which causes brushes to become wedged in the holders. To give some idea of general practice, the following standard tolerances for rectangular and round brushes are presented:

For carbon, graphite and metal-graphite brushes containing up to and including 50 per cent metal by weight:

Length	plus or minus	1/32 inch
Width: over ¾ in.	plus	0.000 inch
	minus	0.015 inch
¾ in. or under	plus	0.000 inch
	minus	0.004 inch
Thickness	plus	0.000 inch
	minus	0.004 inch
Diameter	plus	0.000 inch
	minus	0.004 inch

For metal-graphite brushes containing more than 50 per cent metal by weight:

Length	plus or minus 1/32 inch
Width: over ¾ in.	minus 0.007 inch minus 0.020 inch
¾ in. or over	minus 0.000 inch minus 0.004 inch
Thickness: ½ in. or over	minus 0.007 inch minus 0.011 inch
under ½ in.	plus 0.000 inch minus 0.004 inch
Diameter	plus 0.000 inch minus 0.004 inch

The difference between tolerances on brushes containing under and over 50 per cent metal is due to differences in thermal expansion. Tolerances on holes, shoulders, slots, grooves, notches, etc., are generally considerably more liberal than those shown above. Tolerance on radii, convexing and concaving is plus or minus 10 per cent of radius. On certain allied parts such as conducting washers, bushings, etc., where the shape and design lend themselves to the regular powder-metallurgy procedure of molding, sintering and coining or sizing to finished dimensions, tolerances are similar to such parts as porous bearings and other metal-powder machine parts.

PHYSICAL PROPERTIES OF METAL-GRAPHITE MATERIAL

An approximate idea of the more important physical properties obtainable in metal-graphite materials for brushes and allied parts is presented by the following:

Specific resistance in ohms per inch cube ranges from about 50.0×10^{-5} to 0.4×10^{-5}.

Transverse strength in pounds per square inch varies from about 2500 to 25,000.

Sceleroscope hardness ranges from approximately 5 to 35.

In general, resistivity decreases, transverse strength and hardness increase with increasing metal content. Under conventional operating conditions the coefficient of friction ranges from 0.04 to 0.13 and total positive and negative contact drop ranges from about 0.25 volt to 1.50 volt.

MANUFACTURING ADVANTAGES

For the smaller brushes of relatively simple design, and where volume requirements have justified the development of special equipment and techniques, molding speeds compare favorably with those of other powder-metal parts. Production rates of 1000 pieces per hour and over from a single press are not unusual. Subsequent sintering and finishing operations in these cases have also been developed for speed and low cost. Production speeds of the larger brushes and of the smaller volume items are much slower because practical and economic considerations have not dictated the attainment of higher rates.

The size of lots, which are feasible from a manufacturing standpoint, is considerably smaller than for most other powder-metal products. Dies are not as expensive, being simpler in construction and less precise in dimensions; also die setups require considerably less time. The equipment used to perform the finishing operations is quite flexible and can be quickly set up to handle different sizes and shapes of brushes. All of these factors tend to keep at a minimum the overhead that must be absorbed, and therefore the quantity that can be produced economically may be reasonably small.

In the manufacture of the many and varied products now being produced by the powder-metallurgy method, it has helped to attain such desirable objectives as maintenance of close dimensional tolerances, high production speeds, reduction of scrap or waste, lowered cost, etc. The assumption that it has contributed any single one or combination of these factors to a large degree in the production of brushes does not seem warranted.

On the other hand, and this is true also for certain other powder-metal products, it has produced special structures and made possible the combination and utilization of the desirable properties of certain materials to a greater extent than other methods. This has aided materially in meeting the unusual and more difficult requirements of advanced designs and new types of electrical equipment.

Electrical Contacts Manufactured from Metal Powders

By E. I. Larsen*

Powder metallurgy has been described as being "as old as the pyramids and yet as new as the latest bomber." While this may be true literally, it has been only in the last 10 or 15 years that widespread use has been made of this method of fabricating various articles

One of the first items fabricated by powder metallurgical methods on a commercial scale was electrical contacts, which were fabricated from metal powders as early as 1920. The reason why these contacts have been made for so many years by powder metallurgy is because the compositions of most of these materials are such that they could not be made by the conventional methods of melting, casting, rolling, drawing, etc.

Classes of Contacts

In general, electrical contacts fabricated from metal powders fall into two classes, both from the point of view of the method of fabrication and the components that make up the chemical composition. One class is composed of silver or copper and a refractory metal such as tungsten, molybdenum, or compounds thereof such as carbides. The second class contains a predominant amount of silver and a semirefractory material such as cadmium oxide, nickel, cobalt, or graphite.

Electrical contacts of the first class have been developed primarily as facing materials for heavy-duty circuit-interrupting devices. This class of material unites the high melting point, high boiling point, great resistance to electrical erosion, and the refractory characteristics of molybdenum, tungsten, or their carbides with the high thermal and electrical conductivities and low contact resistance properties of silver or copper.

The second class of material is used for lighter duty or specialized applications such as heavy-duty, direct-current aircraft relays.

Varieties

Electrical contacts fabricated from metal powders are made in a wide variety of compositions, shapes, and sizes. In general, the sizes of electrical contacts fabricated from powders vary from contacts weighing approximately 0.001 oz. up to those weighing 3 to 4 lb., the contacting face being as small as 0.001 sq. in. up to approximately 6 sq. in. in area. The shapes consist of: round or rectangular buttons, some of which have radii or bevels on the contacting faces; rings, cups, rectangular bars, the contact face of which may have a radius across the width and/or at one end; and form-pressed pieces of a wide variety such as angles, both acute and obtuse, irregular shapes comprising a radius blended into a flat, which in turn may have steps.

The size or shape of the contact is dictated principally by the mechanical design of the manufacturer, who in turn may have problems to be met such as: (1) size, weight, or space limitations; (2) electrical conditions such as blowout coils arc chutes, baffles, gas passages.

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The selection of the grade of contact materials depends upon the application. For example, if the contact is to be used as an arcing tip, absolute resistance to welding or sticking is required. If the material is to be used as a current-carrying contact, and is not required to make or break the circuit, factors such as current-carrying capacity and low contact resistance are indicated. In the majority of cases, however, the contact must combine both of these qualities; that is, the material must be able not only to carry the necessary electrical load but also to interrupt or break the circuit when desired. Only by means of powder metallurgy is it possible, at least at the present time, to produce contacts that combine high electrical load-carrying properties with the ability to interrupt the electrical circuit when short-circuit conditions arise.

MANUFACTURE

In nearly all applications the contact is brazed or welded to a copper or copper-alloy backing member.

This operation is important and must be performed with care. Since most metal-powder contacts are somewhat difficult to braze, tinning prior to assembly is recommended. Contact manufacturers prefer to supply parts already tinned. If the contact is thin, overheating must be avoided to prevent the formation of an alloy with the solder and subsequent diffusion of the alloy thus formed into the contact, changing its chemical composition and, as a result, altering its contact characteristics. Any such alteration of the contact is inevitably detrimental to its operating characteristics. Overheating will result also in the oxidation of the refractory constituents. Excess solder must be removed from areas near the contact face, otherwise arcing during operation may cause local fusion. The presence of silver solder on the operating face must be avoided, of course, since this would radically change the characteristics of the contact material.

The manufacture of electrical contacts is immensely more complicated than that of most products made from metal powders for which physical properties and cost are the prime requisites. The prerequisites of contact materials might be listed as follows:

1. High density; that is, a density equal to or approaching the theoretical.
2. Good physical properties.
3. High electrical and thermal conductivity.
4. Low contact resistance.
5. Resistance to welding or sticking.
6. Resistance to electrical erosion.
7. Resistance to corrosion from various atmospheres.
8. Ability to be brazed to other materials.

The necessity for combining all of these qualities in an electrical contact requires extremely careful control throughout the manufacture of the contact, from the selection of raw materials through the attaching of the finished contact to its supporting member in the electrical device in which it is to be used. For example, the powders used in the manufacture of electrical contacts must meet rigid specifications as to purity and particle size. The particle size is measured in microns rather than screen-mesh size. It is extremely important that the powder particles not only fall within a certain range of micron diameters, but that the average particle size in microns and the percentage of particles falling within various groups be constant from lot to lot of powder. If these conditions are not maintained from one lot of powder to another, the final characteristics of the contact materials are radically affected. The contact resistance in one case may be higher, the final composition may be off, the percentage of theoretical density may be low, or the resistance to shock may be low, to mention only a few of the variations that could be expected.

CONSIDERATIONS IN ADOPTING POWDER METALLURGY

The same general rules that apply to other parts fabricated from metal powders hold true for electrical contacts. In a recent article by Carmichael* the following general rules were listed as being helpful in determining whether powder metallurgy could be considered as a possibility for a particular part:

1. Re-entrant angles in the direction of pressing cannot be molded.
2. Holes at right angles to the central axis of pressing cannot be molded.
3. Threads cannot be molded.
4. Parts more than three or four inches in length are prone to weakness of structure in the center, because the pressing is done from the top and bottom only.
5. Parts that require dies of weak construction, such as feather edges, small pins, narrow and deep splines, should be avoided. Powder-metal parts are molded at pressures of 20,000 to 80,000 lb. per sq. in., or even higher, and failures in the dies will occur under these pressures.
6. Bevels and radii should be allowed at all edges and angles, in order to prevent flash marks.
7. It must be possible to construct dies so that, on filling, all powder is placed in the final position, inasmuch as the powdered metal will not flow laterally in the die.
8. Large and sudden changes in cross-sectional area should be avoided.

In thinking of parts being fabricated by powder metallurgy, one visualizes thousands of pieces being pressed at high speeds on automatic presses and sintered in continuous or large batch-type furnaces.

In contrast to this, manufacturers of electrical contacts by powder metallurgy methods think more often in terms of tens and hundreds of pieces. For example, a huge circuit-breaker installation, which costs hundreds of thousands of dollars, may require only a few dozen metal-powder electrical contacts. Thus the contact manufacturer, of necessity, must be able to fabricate relatively small quantities of parts to meet the customer's specific demands. Very often the customer submits drawings of contacts, the design of which has been predicated on his device as a whole and often these designs make work extremely difficult for the contact manufacturer. If a radius could be added here, a small flat there, an angle changed slightly, the thickness to width or length ratio changed somewhat, the contact manufacturer's problems would be immeasurably lessened. Unfortunately, there are no hard and fast rules other than those just mentioned that can be laid down regarding electrical contacts that can or cannot be made with ease by powder metallurgy. If the electrical manufacturer would consult with the contact fabricator when his designs are in the initial stages, much could be accomplished towards form-pressing pieces to finished size and shape, reducing the inventory of powder-pressing dies required, utilizing dies for a variety of different applications and speeding up delivery dates.

Because of the extremely abrasive nature of the refractory materials used in electrical contacts, die life is very short as compared with most other powder metallurgy products. This necessitates the use of special steels and often sintered carbide inserts for punches and dies. Therefore, in order to utilize the simplest type of punch and die design, it is often desirable not to attempt to press an electrical contact to the finished shape but rather approximate this shape and finish the part by machining.

Certain electrical contacts fabricated from metal powders have a limited degree of ductility. This allows for carefully controlled forming operations such as swaging, drawing, and bending. Advantage can be taken of this to produce electrical contacts that would be extremely difficult or impossible to fabricate by form pressing.

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* C. Carmichael: Designing Powder Metal Machine Parts. *Machine Design* (Nov. 1943)

Here, again, the electrical manufacturer and the contact fabricator should work in close collaboration during the initial design stages, to take advantage of these possibilities.

Recent experiments have indicated that some metal-powder compositions can be fabricated into wire and headed.

CONCLUSION

Because of the complexity in the manufacture of electrical contacts by powder metallurgy, I have not attempted to describe in detail the exact procedures, but rather have indicated the importance of two factors:

1. The absolute necessity of rigid control of raw materials and fabricating processes.

2. The necessity of close collaboration between contact users and contact fabricators so that correct contact combinations and the most suitable method of fabricating may be determined before the contact user's final designs have been frozen.

Sintered Magnets

By C. R. Fulton*

The idea of making permanent magnets by sintering is not a new one, but until the introduction of the iron-nickel-aluminum permanent-magnet alloys there was little need for such a process. Permanent-magnet alloys in use up to the time of this development could be forged and machined to the exact size or shape required without too much difficulty. These new Fe-Ni-Al alloys, which have become known as Alnico in this country, soon became very popular because of their superior magnetic properties, but when they were made by casting they did have some disadvantages when compared with the older type of permanent-magnet steels. Among these disadvantages were the following:

1. It was almost essential that they be cast to size, since they could not be readily forged or machined. The material could be ground but this was quite expensive, particularly for small magnets in large quantities.

2. The material had a large grain size and was mechanically weak.

3. Close tolerances could not be held and on small magnets this meant grinding almost the entire magnet. Because of the brittle nature of the material, there was considerable loss due to chipping and cracking during these grinding operations.

4. Because of its high aluminum content, the molten alloy had a high surface tension. It was difficult to prevent loss of aluminum by oxidation during the melting operation.

In view of these difficulties it is not hard to understand why a process for sintering alnico was developed, or why sintered alnico has come into such widespread use in recent years. It might be well to qualify this by saying that it has come into widespread use for small magnets weighing 2 oz. and less, of the type shown on Fig. 1. In this size range, sintered alnico has been able to compete in price with cast alnico. Magnets larger in size, of the type shown on Fig. 2, can be made but they do not compare favorably in price with the cast material. An idea of the range of sizes that have been produced is given by Fig. 3, which shows a small magnet weighing 0.006 oz. and a large magnet with a steel insert weighing 4 lb., both made from sintered alnico. Magnets weighing more than 2 oz., however, should not be made from sintered

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alnico unless some of the properties of the sintered magnet are required.

It is only in the smaller sizes, where the material cost is not such an important factor, that sintered alnico can be made to compete with cast alnico; also, the smaller magnets lend themselves to high-speed production equipment better than the larger sizes. The process of making sintered magnets is inherently one for high production, and all the equipment has been designed and constructed with this idea in mind; single orders for 500,000 magnets of one type are not uncommon.

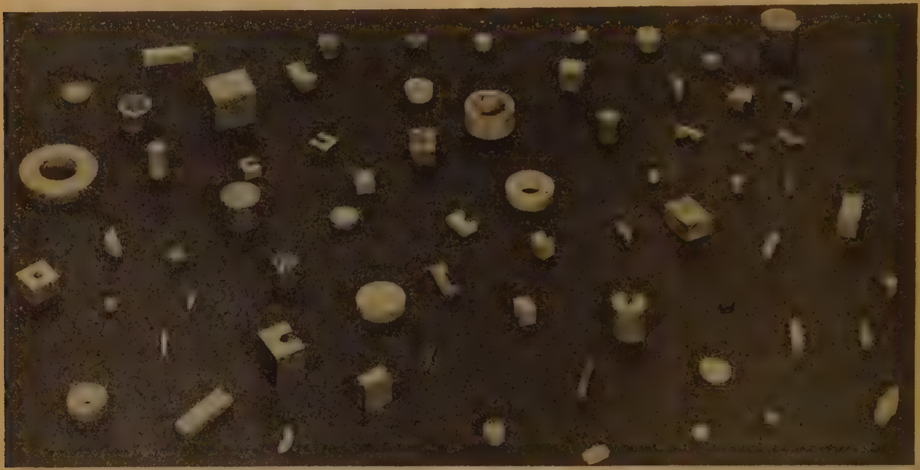

FIG. 1.—SMALL SINTERED MAGNETS THAT ARE PARTICULARLY ADAPTABLE TO THE SINTERING PROCESS (UNDER 2 OUNCES).

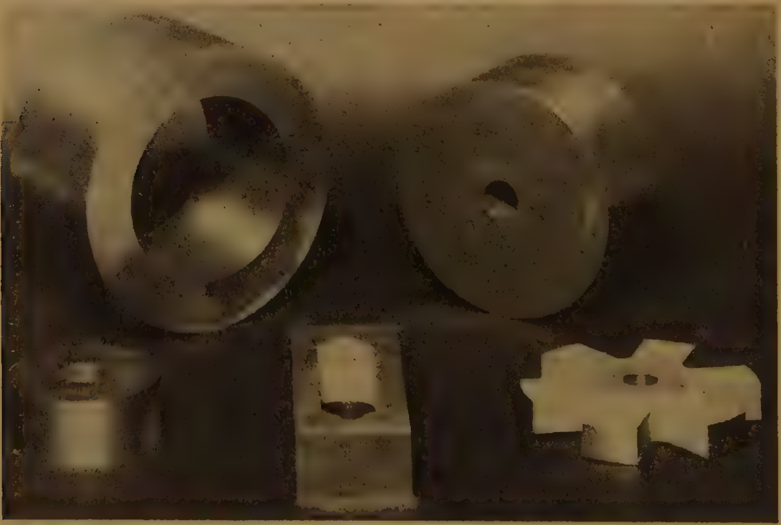

FIG. 2.—LARGE SINTERED MAGNETS THAT MAY BE PRODUCED BY SINTERING (UP TO 4 POUNDS).

ADVANTAGES OF SINTERED ALNICO

Sintered alnico has the following advantages over similar alloys made by conventional casting methods:

1. Small intricate-shaped magnets can be sintered to size with little or no grinding.

2. Close tolerances can be maintained.

3. The material is fine grained and is approximately three to five times as strong as cast alnico.

4. The material is free from cracks, cold shuts, and segregation of impurities at the grain boundaries and, as a result, there are no consequent poles produced by physical imperfections. These properties also result in a more uniform flux distribution.

5. Compositions can be held to very close limits.

6. It is possible to place a steel insert in the pressed magnet and then sinter the insert firmly in place while performing the regular sintering operation. Fig. 4 shows the various steps of this operation. The insert does not melt or become hardened during the sintering operation, nor is the magnet appreciably weakened by cracks or strains as the result of its shrinking around the insert. The insert may be readily machined after sintering. Fig. 5 shows several sizes of magnets in which steel inserts have been sintered in place. These magnets are all of the rotor type and the steel insert makes the mounting of them on a shaft a simple matter. Sintered alnico magnets of this type are ideal for high-speed applications where the forces encountered prohibit the use of cast alnico.

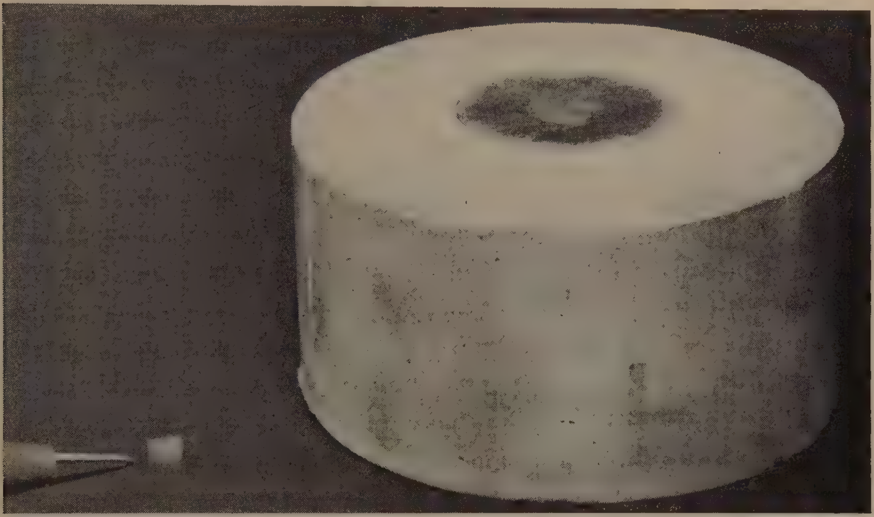

FIG. 3.—COMPARISON IN SIZE OF LARGEST (4 POUNDS) AND SMALLEST (0.006 OUNCES) SINTERED MAGNETS BEING MADE AT PRESENT TIME.

In addition to these advantages, sintered alnico has practically the same magnetic properties obtained with cast alnico.

SINTERING PROCESS

While it is not the purpose of this paper to go into any great detail in regard to the manufacture of sintered alnico, a brief outline of the steps involved will probably be of interest:

1. The constituent powders, in the correct proportions, are mixed by tumbling.

2. The mixed powders are then compressed by either a high-speed mechanical press or a hydraulic press. While it is desirable to press the magnet to the required size and shape, with suitable allowances for shrinkage, it is possible to make small quantities or sample magnets by machining the magnets from partially sintered bars, plugs or cylinders. These are pressed up in stock dies. Magnets made by this method are relatively expensive as

compared with those pressed to the exact size required. Pressures in the order of 60,000 lb. per sq. in. are used and the pressed density runs from 5.30 to 5.85 grams per cubic centimeter. The dies used are made from alloy steel and some have Carboloy liners. These dies are quite expensive, the average cost being about $250—the cost of individual dies varies from $100 to $500, depending on the complexity of the piece. Figs. 6, 7, and 8 show some of the various types of dies employed, together with the magnet pressed in each.

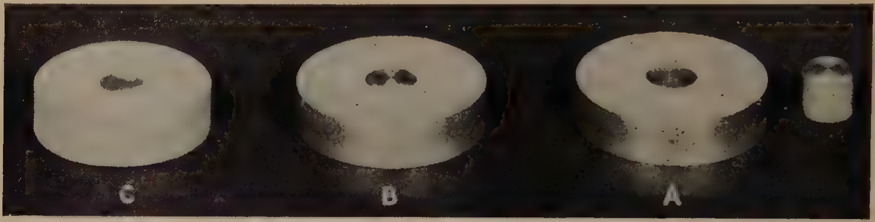

FIG. 4.—STEPS IN MAKING SINTERED MAGNETS WITH STEEL INSERT.
A, pressed magnet with knurled steel insert.
B, pressed magnet with steel insert dropped in place ready for sintering.
C, sintered magnet.

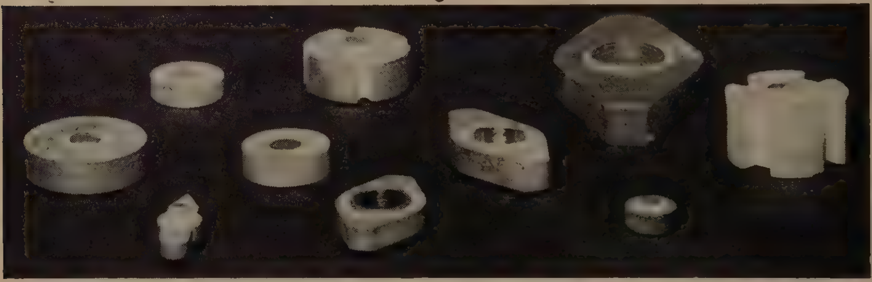

FIG. 5.—EXAMPLES OF SINTERED MAGNETS WITH STEEL INSERTS.

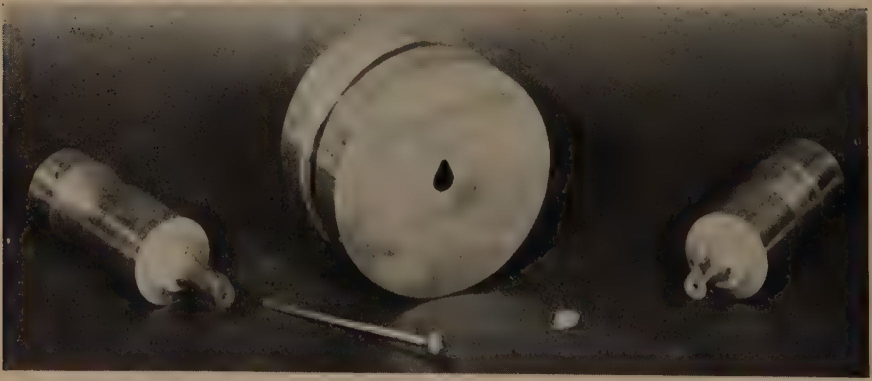

FIG. 6.—DIE FOR HYDRAULIC PRESS WITH SAMPLE OF PRESSED MAGNET.

3. The pressed magnets are then sintered in a specially designed continuous furnace, in an atmosphere of pure dry hydrogen. The pure dry hydrogen is made necessary by the high aluminum content of the alloy; any oxidation of the aluminum

retards diffusion and results in a porous magnet of inferior magnetic properties. During the sintering operation, the magnet shrinks from 2 to 10 per cent, depending upon the composition, sintering temperature, particle size and particle-size distribution of the powders, and the pressure employed during pressing. To obtain a thorough interdiffusion of the constituents during the sintering operation, temperatures close to the alloy's melting point must be employed if a satisfactory product is to result.

4. If the heat-treatment is not a part of the sintering cycle, as it usually is for the smaller magnets, the magnets must be heat-treated—preferably before the magnet is ground.

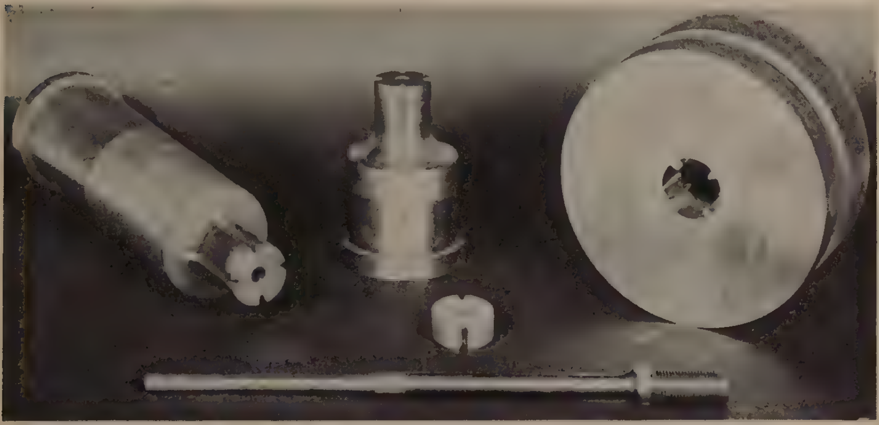

Fig. 7.—Large die for tablet machine with pressed magnet.

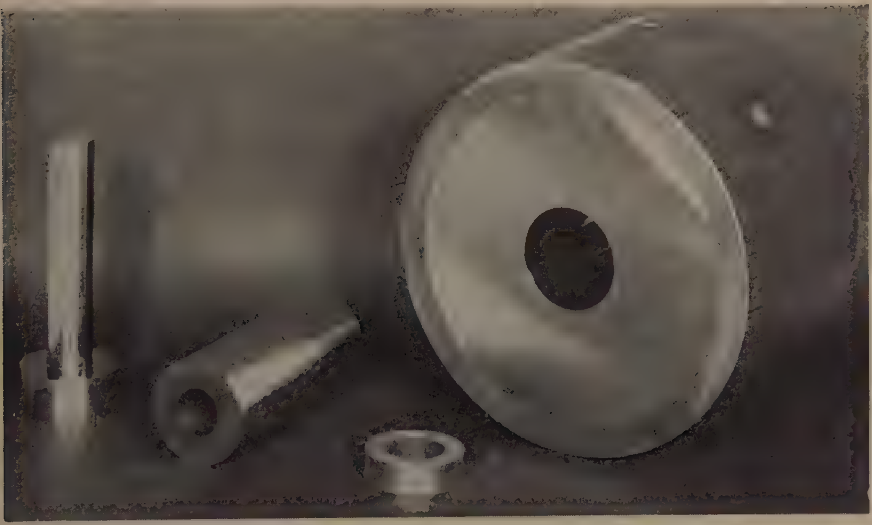

Fig. 8.—Small die for tablet machine, with pressed magnet.

Design

The simplest form of die employed in the pressing of sintered magnets is illustrated in Fig. 9. It consists of a die shell, top and bottom punch. In addition to these parts a core pin will be required for each hole in the magnet.

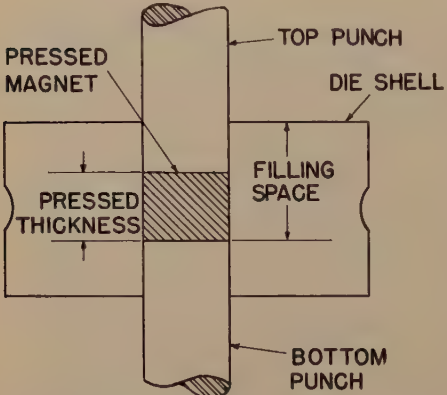

Fig. 9.—Basic parts of die for pressing magnets.

The ratio of filling space to pressed thickness (Fig. 9) is about 2½:1 for alnico powder. The pressed thickness of the magnet can usually be varied within a fairly wide range; this is illustrated in Fig. 10, which shows cylindrical magnets of various thicknesses, all pressed in the same die. The thickness of all the magnets shown on Fig. 11 can be varied in the same manner. Fig. 11, incidentally, is just another view of Fig. 1, which was taken looking directly down on the magnets as pressed.

In most cases it is desirable to use this type of die in a press in which the metal powders are automatically deposited in the die cavity, the correct amount of powder being determined by the filling space; the pressing and ejection being controlled by cams so that the whole cycle of operation is properly synchronized. Mechanical presses of this type are available that will press up to 200 pieces per minute. Pressure may be applied only by the top punch, while the bottom punch remains stationary, or in some cases pressure may be applied by both top and bottom punch.

In view of the fact that the flow characteristics of metal powders are poor, the die must be designed so that a uniform pressed density will be secured throughout the magnet, otherwise shrinkage will not be uniform. The shape of the magnet must lend itself also to easy ejection from the die by the bottom punch. Since the die usually operates only in the vertical direction, undercuts and cross holes are not feasible; side or pull pins cannot be used. The powders employed in pressing sintered alnico are very abrasive and difficult to press under ideal conditions. In view of this, and the high pressures employed, the die should be kept as simple as possible, otherwise excessive breakage and the high cost of maintaining the die will materially increase the cost of the finished magnet. The initial cost of the die, as well as its maintenance, will, to a large extent, be governed by the number of magnets that are to be produced. In any event the construction of the die should be as strong and simple as possible; the number of moving parts should be kept at a minimum. Ejec-

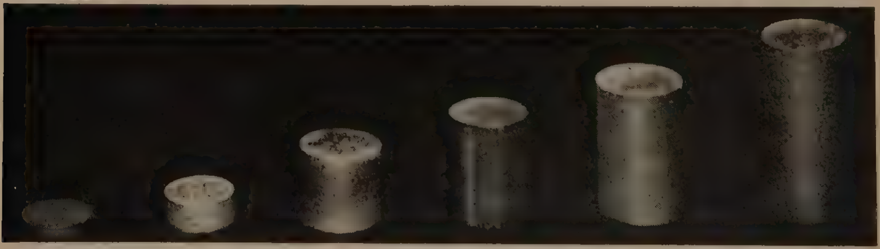

Fig. 10.—Sintered magnets of various thicknesses all pressed in same die.

tion pressure and laminations are generally minimized by lapping the die in the direction of pressing or chromium plating.

The expense of making a die for less than 5000 magnets is not usually justified, although some dies are made for as few as 250 magnets. Here again it is difficult to establish a firm rule, as the cases vary so widely. In one case, where the sintered magnet is competing on an equal basis with a cast magnet, and the only criterion is price, the die cost is an important factor; in another, where the magnet can be made only by sintering, the die cost is not so important.

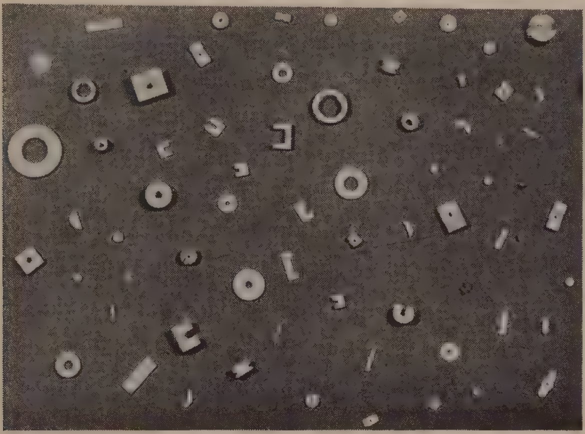

FIG. 11.—ANOTHER VIEW OF FIG. 1 LOOKING DOWN ON MAGNETS AS THEY WOULD BE EJECTED FROM DIE.

Size Limitations

Maximum and minimum dimensions are as follows:

Maximum length (in direction of pressing), in.	2
Minimum length (in direction of pressing), in.	0.080
Maximum cross section, sq. in.	2
Minimum cross section, sq. in.	0.010
Maximum weight, oz.	2
(Where cost is not a factor, sintered alnico magnets have been made up to 4 lb.)	
Minimum weight, oz.	0.006
Minimum diameter of hole, in.	0.080

It is necessary to keep in mind that there is a maximum length for each cross-sectional area; if this is exceeded, excessive shrinkage will result and close tolerances cannot be held. While no exact rule can be given, the pressed length should not, in general, exceed three times the smallest cross section.

Tolerances for Sintered Alnico

DIMENSIONS UP TO	INCH
⅛ in. inclusive	±0.005
⅛ to ⅝ in. inclusive	±0.010
⅝ to 1¼ in. inclusive	±0.015
1¼ to 3 in. inclusive	±0.031
Over 3 in.	±0.062

It should be kept in mind that these are as-sintered tolerances and that this alloy cannot be coined or sized to the close tolerances that are obtained with some other types of metal-powder products.

PHYSICAL PROPERTIES

Sintered alnico has a relatively low density, 0.25 lb. per cu. in. It is relatively weak and brittle, as compared with other types of permanent-magnet alloys. As mentioned earlier in the paper, it cannot be readily forged or machined and usually is ground to size. It can be cut with a wet, abrasive wheel under proper conditions.

In grinding or cutting sintered alnico, a wheel that breaks down fairly rapidly should be used and the operation is preferably done wet—care should be taken not to overheat the material. It should be kept in mind that sintered alnico, because of its fine grain, cannot be ground and cut with exactly the same wheel as that used for the cast material.

Sintered alnico has approximately three to five times more resistance to transverse fracture than cast alnico. The transverse modulus of rupture for sintered alnico averages 70,000 lb. per sq. in. The Rockwell hardness is 45 to 50-C.

SUMMARY

The designer of a product using sintered magnets should keep in mind the following points in order to secure the most satisfactory product for the minimum cost:

1. Avoid close tolerances that are not necessary.
2. Avoid thin sections in the magnet at any point—they will cause nonuniform shrinkage and also will usually cause warpage during sintering.
3. Avoid designs that require sharp feather edges on the punches or small holes.

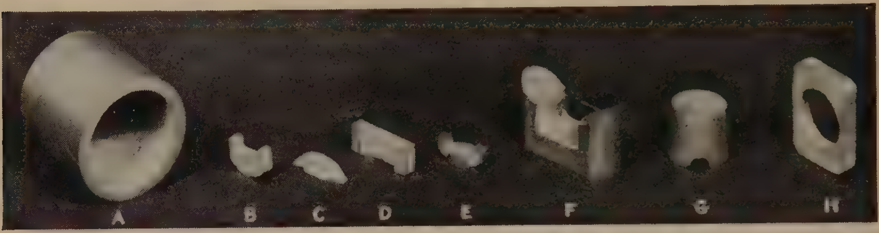

FIG. 12.—TYPES OF MAGNETS THAT ARE DIFFICULT OR IMPRACTICAL TO MAKE BY SINTERING.
A, cross section too small for diameter and length.
B, cross section too small at poles.
C, nonuniform thickness in direction of pressing.
D, cross section too small for length.
E, nonuniform thickness in direction of pressing.
F, sharp feather edges, nonuniform thickness in direction of pressing.
G, tapered and nonuniform thickness in direction of pressing.
H, too thin a section.

4. Avoid undercuts or holes not parallel to the axis of pressing.
5. Avoid blind holes or counterbores in the direction of pressing.
6. Try to keep a uniform thickness in the direction of pressing.
7. Avoid tapers in the direction of pressing.
8. Do not make the magnet too long in the direction of pressing, in proportion to the area of cross section.
9. Take the manufacturer of the sintered magnet into your confidence. He may be able to make valuable suggestions. On new designs give him complete details in regard to the problem and the limitations.

Several of the objectionable features outlined above are shown on Fig. 12. This shows eight different types of magnets that either gave trouble in pressing or in which excessive warpage occurred as a result of the sintering operation.

Friction Articles from Metal Powders

By C. T. Cox,* Associate Member A.I.M.E.

The title of this short paper necessarily implies that friction articles comprise a distinct and unique field and are different from the other metal-powder articles, such as bearings, electrical contacts, and magnets. However, this distinction is rather hard to define in that it is really one of degree and not of kind. It would appear that the main distinction is that friction articles are articles of rather large pressing area. In other words, they are articles in which the area of the mold in which the metal powder is pressed is relatively large. Other articles made from metal powders are generally of rather small area, usually a few square inches, while in friction articles the area ranges up to several hundred square inches.

The satisfactory production of metal-powder friction articles involves many production problems and a large number of these are accentuated by the large area. Since it is impossible in the short space of this paper to describe adequately all the problems involved, I have thought it best to merely mention some of them and to place particular emphasis upon a problem that is common to all metal-powder articles, although it is of greater importance in the making of friction articles. This problem has to do with the effect on the properties of a friction article of small variations in the composition. However, before discussing the problems, it is probably appropriate that some mention be made of the limitations on the use of friction articles.

Limitations

Most engineers are familiar with the general field that can be characterized as constituted by clutch facings and brake linings, and undoubtedly have heard many stories of how metal-powder friction articles have had a service life 10 times as long as nonmetallic friction materials, and of instances where metal-powder friction articles have operated satisfactorily where no other material could be used. These instances should not be regarded as criteria for the assumption that metal-powder friction articles are capable of universal use in the friction field and will always outperform other materials. On the contrary, metal-powder friction articles are unsuitable for numerous applications, either on a performance or on a cost basis.

Metal-powder friction articles will not replace wooden block brakes for wagon wheels nor cast-iron brake shoes for railway car wheels, to mention just two obvious examples. Metallic friction articles cannot be used where they must act as heat insulators, for they have a relatively high thermal conductivity as compared with asbestos. This is a detriment in some uses, as in certain airplane brakes having hydraulic actuators provided with rubber seals. The metallic friction material readily transfers the heat developed at the braking surface back through the material to the rubber seal and destroys it.

Within its limited field, metal-powder friction material has proved satisfactory, but many problems are involved in the selection of the proper material to use in an application and in the commercial pro-

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* S. K. Wellman Company, Cleveland, Ohio.

duction by a manufacturer of the selected material.

Obtaining Adequate Strength

One of the problems is that of obtaining adequate strength in the article and this is accentuated by the relatively large area. As is known, sintered metal powders do not have a tensile strength comparable with that of solid metal, and the presence of nonmetallic materials such as graphite and silica further weakens them. In addition, because of considerations of cost and weight, it has been found generally necessary to have the sintered metal powder of relatively small thickness in relation to its area. These factors have required the presence of a reinforcing member of solid metal to which the sintered powder is integrally secured (as by brazing or welding) in order to obtain the requisite mechanical strength.

The necessity for a backing member creates production problems involving the briquetting of the powder and the assembling and heat-treating operations. Generally the powder is briquetted and placed on the backing and then heated so as to cause the metal powders to sinter and to braze to the backing member. However, the higher temperature necessary for brazing raises the problem of the sweating of lead, if it is used, and the deleterious annealing and lowering in strength of the solid metal backing member.

The large area of the friction material complicates the briquetting operation. For example, the charge of powder for each briquette must be measured by weighing rather than by volume, as is customary in automatic briquetting machines, and must be carefully spread in the mold in order that the pressed and sintered article may be of uniform thickness and density. It is desirable that all metal-powder articles be produced to finished size and shape, and this is almost imperative in making friction articles, as the large area makes sizing and subsequent machining exceedingly expensive.

Selection of Mixture

Another and major problem in this field, as in other metal-powder fields, is the selection of a mixture of metal powders that is suitable for a specific application and the determination of the proper pressing and sintering techniques to obtain optimum properties. It is an established fact that a mixture satisfactory for one application may be totally unsuitable for another application involving different speeds, pressures, and temperatures. Thus, a mixture suitable for an airplane brake is usually unsuitable for an automobile brake, and in a selected mixture small variations in amounts of ingredients or the particle size thereof will greatly change the characteristics.

I have selected this latter problem of the effect of variations in composition on the characteristics of the sintered friction article as the one that will receive specific attention here.

Effect of Variations in Composition

Small variations in composition affect not only the metallurgical but also the physical characteristics of the mixture and the manner in which the metal-powder friction article performs. These variations affect the value of the coefficient of friction, strength, wear (both of the material and the engaging surface), the allowable unit pressures and heat development, the noise or quietness of the material in use, and the rate of change of the value of the coefficient of friction with changes in unit pressure, temperature, and speed. Since the usual metal-powder friction material is made up of from four to eight separate ingredients, and a change in any one of these will affect the result, there are innumerable opportunities for experimentation.

This may best be understood by reference to a specific example. One mixture that is satisfactory comprises:

	Parts by Weight
Copper	76
Tin	6
Lead	10
Iron	8
Silica	5
Carbon	8
	113

This material has a satisfactory coefficient of friction at slow engagement speeds and the drop in coefficient of friction with increase in speed is not too great. The material is also quiet and the wear is not excessive. If the amount of graphite is increased from eight to nine parts, the coefficient of friction at slow engagement speeds drops from 0.50 to 0.45, and the material becomes slightly more noisy in use; otherwise, it is satisfactory. If the graphite is now increased to 10 parts, the coefficient of friction drops to a value of 0.39 and the wear has become excessive. If in this last composition we increase the amount of SiO_2 from five to six parts, the coefficient of friction increases to 0.54, and the wear is satisfactory. It should be observed that these numerical values for coefficient of friction are not absolute and are used only for comparative purposes.

Corresponding changes in results are attained by varying the amounts of the other ingredients. Thus, if in our initial mixture referred to previously, the amount of iron is decreased from eight to three parts, the coefficient of friction drops from a value of 0.50 to 0.37, and the material becomes somewhat noisy in operation. On decreasing the amount of iron to one part, it would be assumed that this change would be accentuated, and this is true in that the value of the coefficient of friction decreases. However, unexpectedly, the material is no longer noisy but becomes quiet in operation; although the wear is rather excessive.

When it is realized that these changes have resulted from varying the amount of only one or two ingredients of the mixture, and that there are six ingredients that may be varied in amount as well as in shape and size of the particles of the powder used, and that the value of the coefficient of friction varies with unit pressure, temperature, and speed, it is seen that the selection of a mixture suitable for a particular application is rather difficult. This, however, is merely one of the numerous problems. The selection of the processing techniques that are to be used is, of course, another and major problem and the large area of friction articles accentuates these problems.

Field of Usefulness

With the suitable field of use of metal-powder friction articles limited to such narrow scope, and with production of uniform articles exceedingly difficult, it would seem that metal-powder friction articles are a relatively minor and useless field of endeavor. However, metal-powder friction articles have been used in applications where they operate at temperatures up to 1700°F. and under unit pressures of 500 lb. per sq. in. in brakes to absorb up to 3,000,000 ft-lb. of energy. They have operated often in automotive clutches for one hundred thousand miles of satisfactory service and have given extraordinarily satisfactory service in airplane brakes and supercharger clutches. In their own limited field and for the particular applications for which they are suitable, metal-powder friction articles are supreme, and will continue to do a satisfactory job in these fields and in related fields if the existing limitations are constantly observed.

DISCUSSION

(F. N. Rhines presiding)

W. A. Reich.*—I should like to ask Mr. Cox if he has any information on the change in coefficient of friction in a metallic clutch plate with a temperature range of minus 40°F. to 200°F. Do metallic friction materials have an advantage over conventional nonmetallic materials in that regard?

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* General Electric Co., Schenectady, N. Y.

C. T. Cox.—The best that we can tell is that any application merely involves two surfaces, pressures, temperatures and the coefficient of friction no matter how you measure it. What I attempted to show is that we can have a mix that will operate under certain conditions but it may not be good for other conditions.

As to applications for a mix that would be satisfactory at higher temperatures, I think I might illustrate that best by reference to a rather general installation, the airplane brake. At the present time a large percentage of the airplanes use a metallic disk as a braking element and many of these operate at relatively high temperatures. So far as we know in the laboratory, about 1000° or 1100°, is the top temperature that we recommend for service installations. Does that cover it?

W. A. Reich.—In certain torque-limiting clutches that we make the necessity is to find a material that gives uniformity of torque output over a range of temperatures.

C. T. Cox.—You mean it would be constant regardless of the rise in temperature?

W. A. Reich.—That is right.

C. T. Cox.—To my knowledge there is no material that has a constant coefficient of friction with variation in temperature. You merely approach that, and how close you approach it depends on what you want.

W. A. Reich.—I am speaking of the rather limited range of minus 40° up to 200°F.

C. T. Cox.—Within that range I do not believe there is any question but that some of the metallic friction mixtures are satisfactory.

W. A. Reich.—Do you mean with a variation of 10 or 5 per cent?

C. T. Cox.—I do not have the figures. I can give you an illustration to get it down to something we can all understand. The simplest thing that we are familiar with is an automobile. To our knowledge there has been no satisfactory metal-powder friction material for an automobile brake. Many materials look good, but cannot be used in commercial practice. An ordinary mix will work well on an automobile if you want to stop for anything up to 50 miles an hour. The coefficient of friction will decrease with increasing speeds of stop. In some mixtures it occurs at 60 miles an hour and the coefficient of friction has dropped from a value of 0.35, value to very near to 0.1, which means that the driver has to be about 6 ft. high, slide down on his seat and get his shoulders against the back in order to stop the car.

Research Papers

(*E. E. Schumacher and F. N. Rhines presiding*)

The program of the afternoon session was opened by presentation of the paper by F. R. Hensel and E. I. Larsen, as follows:

Certain Characteristics of Silver-base Powder Metallurgical Products

By F. R. Hensel,* Member A.I.M.E., and E. I. Larsen†

The present paper describes a number of experiments with fine silver, coin silver, silver-cadmium oxide and silver-nickel-copper compacts, prepared by powder metallurgical methods. The test data are of a preliminary nature, since most of the work was exploratory.

Fine Silver

Effect of Compacting Pressure on Hardness and Density during Cold and Hot Pressing

The cold-welding properties of silver have received considerable attention and the welding characteristics are functions of such variables as: cleanliness of metal particles (impurities and adsorbed gases), chemical nobility of particles, plasticity and hardness, particle assortment, particle shape, particle porosity, apparent density, temperature, pressure, time, recrystallization characteristics.

Chemical nobility, plasticity and low temperature of recrystallization after work-hardening are responsible for the excellent low-temperature bonding properties of silver.

Several series of compacts were pressed at pressures of 5, 10, 20, 30, 40, 50, 60 70 and 80 tons per square inch, at temperatures of 32°C. (room temperature), 100°, 200°, 300°, 400°, and 450°C. Silver powder of minus 325-mesh, produced by displacing silver from a nitrate solution by means of copper, was used. The density was calculated from accurately measured and weighed compacts. The hardness was measured on the Rockwell F scale.

The investigation shows that an increase in pressure promotes a higher density and hardness regardless of pressing temperature, up to a temperature of 400°C. The pressure-density curves at various pressing temperatures are shown in Fig. 1, the pressure-hardness curves at various pressing temperatures, in Fig. 2. The greatest increase in both hardness and density was obtained in the pressure range of 5 to 20 tons per square inch.

A compact from each series was annealed at 300°C. in air, for various lengths of time. The hardness values after annealing are shown in Table 1.

Table 1.—*Hardness of Compacts Annealed at 300°C.*

Rockwell F Scale

Sample No.	Treatment, 80 Tons per Sq. In. at	Sample Pressed	Sample Annealed 1 Hr.	Sample Annealed 2 Hr.	Sample Annealed 4 Hr.
#1	32°C.	84	40	40	40
#2	100°C.	85	44	42	41
#3	200°C.	84	42	42	42
#4	300°C.	84	40	40	40
#5	400°C.	76	40	40	40
#6	450°C.	78	38	37	38

A minimum hardness was obtained after one hour of annealing. No change in density occurred during annealing. The maximum density was obtained at 80 tons per sq. in., and at this pressure the hardness is equal to that of hard-drawn wrought

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* Consulting Engineer, P. R. Mallory and Co., Indianapolis, Indiana.

† Manager, Metallurgical Research Department, P. R. Mallory and Co.

silver (85 Rockwell F scale), as long as the pressing temperature does not exceed 400°C.

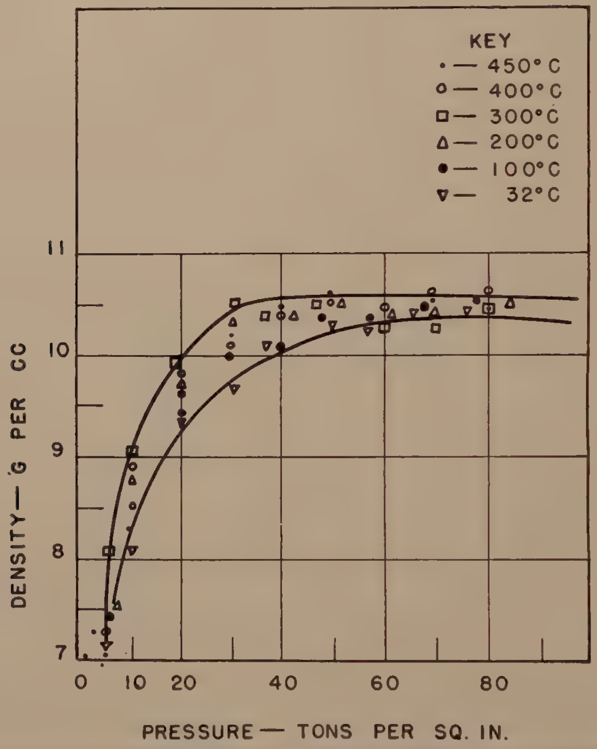


Fig. 1.—Density of silver-powder compacts after pressing at various pressures in a die heated at temperatures from 32° to 450°C.

These data do not indicate unusual hardness characteristics during hot-pressing, as has been observed with gold and copper.

The speed of compacting must be taken into consideration in the interpretation of the results given above, and it is to be expected that the hardness of the compacts compressed at elevated temperatures will be lower as the pressing speed is decreased, since partial annealing might take place.

The tensile properties of silver when tested at temperature drop with increasing temperature linearly up to about 160°C. and a sharp drop occurs between 200° and 250°C. Compressing in these ranges therefore should provide the highest plasticity, however the factors of compacting speed and impossibility of instantaneous recrystallization result in properties that are hardly different from those obtained when pressing is carried out at room temperature.

Effect of Sintering Conditions on Density of Fine Silver Compacts

It has been noted on previous research with silver powder and silver-powder alloys, that compacts show expansion with resintering or solution treatments as a result of inadequate initial sintering. The purpose of these experiments was to determine the effect of initial sintering periods on the final volume changes of compacts pressed, sintered, repressed and resintered. The curves in Fig. 3 show the volume change of the repressed compacts after resintering versus the length of time for which they were originally sintered.

It was found that as the pressed density was increased the length of time necessary to cause complete sintering increased.

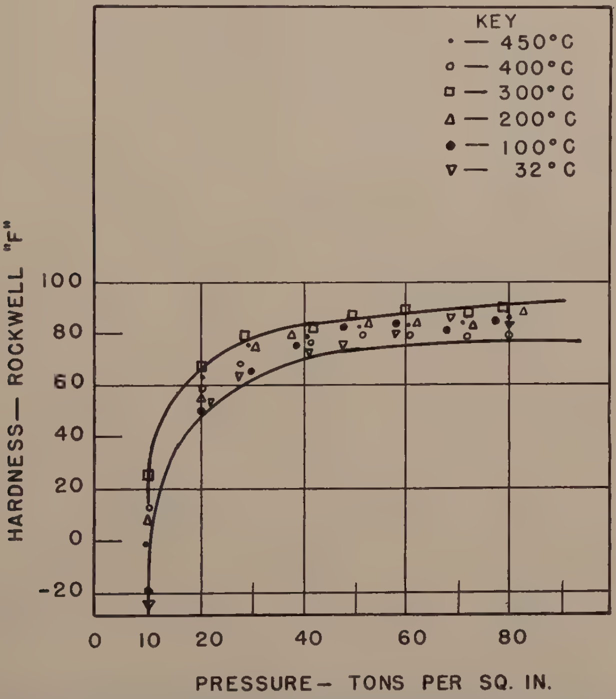


FIG. 2.—HARDNESS OF SILVER-POWDER COMPACTS AFTER PRESSING AT VARIOUS PRESSURES IN A DIE HEATED AT TEMPERATURES FROM 32° TO 450°C.

The sintering and resintering was carried out in air atmosphere. While in Fig. 3 the relative volume changes are plotted, some of the actual density values are cited in Table 2, to present a more complete picture. These results are somewhat surprising. In wrought silver the density depends upon its mechanical state. In the annealed condition it is generally given at 10.49 grams per c.c. while in the cold-worked condition it is lower and a density of 10.43 grams per c.c. is the accepted value. When measured at elevated temperatures such as 800°C., the value is 9.80 grams per cu. centimeter.

In sintered compacts, the density conditions are much more complex. It is quite possible that during pressing at high pressures gases will be entrapped, and in a ductile material such as silver will be sealed into the compact by cold-welding of the

TABLE 2.—*Densities of Silver Compacts after Various Treatments*

GRAMS PER CUBIC CENTIMETER

Initial pressure, tons per sq. in.	12.5	25	50
As pressed	8.3	9.06	10.15
As sintered at 880°C.:			
For 1 hr.	9.45	7.44	7.36
4 hr.	9.09	7.59	7.06
7 hr.	9.17	7.36	6.01
Repressed at 50 tons	10.32	10.35	10.10
Resintered for 2 hr. at 850°C.:			
1 hr. original sintering time	10.03	8.9	8.61
4 hr. original sintering time	10.10	10.03	9.51
7 hr. original sintering time	10.06	10.28	9.74

silver particles. In compacts of high initial density, diffusion of these entrapped gases through existing voids is impossible, therefore in heating the compacts will expand because of the forces exerted by the expanding gases. It might be possible to prove this point definitely by pressing compacts under vacuum. The speed with which compacts are heated to the sintering temperature and the length of time at sintering temperature has a direct bearing on the amount of entrapped gases retained in the sintered compact. If the sintered compacts are repressed, the remaining entrapped gases are recompressed. The expansion of the entrapped gases during resintering again causes a decrease in density.

An important factor is the original amount of gases present in the pressed powder compact, the pressing speed, the dimensions of the piece pressed, the pressure dwell after pressing and the construction of the die.

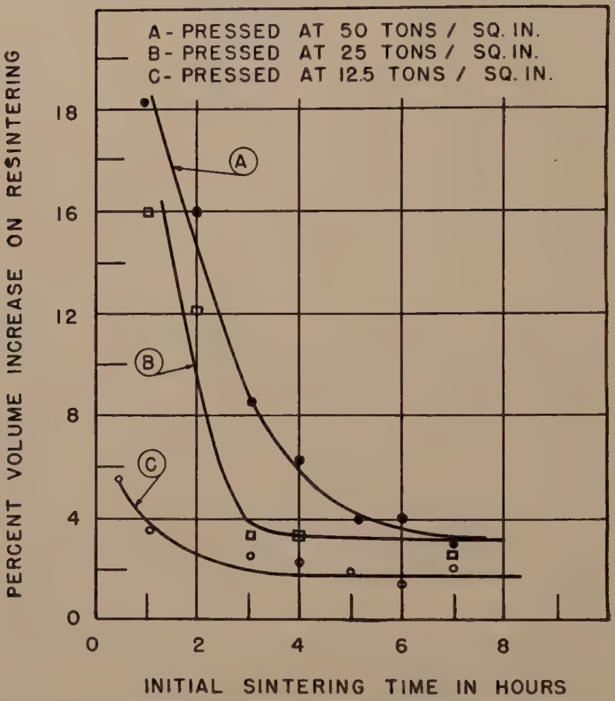


FIG. 3.—EFFECT OF INITIAL SINTERING TIME ON FINAL DENSITY OF SILVER-POWDER COMPACTS. Pressed at 12.5, 25 and 50 tons per inch, sintered from 1 to 7 hours at 880°C., repressed at 50 tons per inch and resintered at 850°C. for 2 hours.

Effect of Sintering Atmosphere (Hydrogen or Air) on Physical Properties of Fine Silver Compacts

The data shown in Tables 3 and 4 can be summarized as follows:

1. The density of silver compacts when sintered in air is considerably higher than the density after sintering in hydrogen. Correspondingly, the physical and electrical properties of the compacts sintered in hydrogen are lower. The following explanation of this phenomenon is offered:

During pressing of the silver compacts, a quantity of air is entrapped in the pressed compact. When the compact is sintered in hydrogen, the latter will react with the entrapped oxygen to form water vapor, thereby greatly increasing the volume of gas. This phenomenon is generally known as hydrogen embrittlement, and when it occurs in wrought materials, blistering, fracturing and internal cracks result.

TABLE 3.—*Effect of Sintering in Air on Physical Properties of Fine Silver Compacts*

Treatment	Density, Grams per C.C.	Ultimate Tensile Strength, Lb. per Sq. In.	Electrical Conductivity, Per Cent I.A.C.S.
Pressed at 10 tons per sq. in. sintered for 2 hr. at 900°C........	9.61	15,450	91
Pressed at 10 tons per sq. in., sintered for 2 hr. at 900°C., repressed at 50 tons per sq. in...........	10.02	31,600	97.2
Pressed at 10 tons per sq. in., sintered for 2 hr. at 900°C., repressed at 50 tons per sq. in., annealed 2 hr. at 400°C.......	10.02	24,200	101

TABLE 4.—*Effect of Sintering in Hydrogen on Physical Properties of Fine Silver Compacts*

Treatment	Density, Grams per C.C.	Ultimate Tensile Strength, Lb. per Sq. In.	Electrical Conductivity, Per Cent I.A.C.S.
Pressed at 10 tons per sq. in., sintered for 2 hr. at 900°C.........	7.80	7,780	69
Pressed at 10 tons per sq. in., sintered for 2 hr. at 900°C., repressed at 50 tons per sq. in..........	10.01	33,500	94.4
Pressed at 10 tons per sq. in., sintered for 2 hr. at 900°C., repressed at 50 tons per sq. in., annealed 2 hr. at 400°C. in air.	10.05	24,050	101

2. After repressing, the physical and electrical properties of materials sintered either in air or in hydrogen are practically identical.

3. Annealing at low temperatures in air decreases the tensile properties and increases the electrical conductivity, as would be expected.

COIN AND STERLING SILVER COMPACTS

Initial Tests on Sterling Silver Compacts

The initial experiments show that it is not readily possible to make sound, homogeneous sintered compacts from a mechanical mixture of silver and copper powders. This conclusion was based upon a microscopic examination of the sintered compacts, which showed small areas of the copper-silver eutectic in a matrix of silver. Also, if the copper had gone into solution in the silver, the sintered compacts should have responded to precipitation-hardening. In some, very slight hardening occurred, but in most samples no hardening was noted. Sintering was carried out in a hydrogen atmosphere above and below the eutectic silver-copper temperature for times at temperatures ranging from 1 to 4 hr. Various aging temperatures were tried, ranging from 225° to 325°C. for periods ranging from ½ hr. to 3 hours.

Tests on Coin and Sterling Silver Compacts Using Alloy Powders

Materials.—The coin and sterling powders used for this investigation were made by an atomizing process, which caused each powder particle to be spherical. The photomicrograph in Fig. 4 shows the particle shape. The data on the physical characteristics of the powders are given in Table 5.

TABLE 5.—*Physical Characteristics of Coin and Sterling Silver Powders*

Powder	Screen Mesh	Percentage Retained on Screen	Scott Volumeter Density, Grams per Cu. In.	Tap-weight Density, Grams per Cu. In.
Coin silver—10 per cent copper, 90 per cent silver.	150	0.7	96.7	108.1
	200	32.6		
	270	28.1		
	325	10.1		
	Pan	27.6		
Sterling silver—7.5 per cent copper, 92.5 per cent silver.	150	1.2	96.4	105.5
	200	27.5		
	270	26.0		
	325	11.0		
	Pan	33.7		

Pressing.—It had been noted previously when compacting and sintering of silver and silver-base alloys that a low compacting pressure yields the best sintered compacts. For this reason, all the compacts made of the powders used in these tests were pressed at a pressure of 10 tons per sq. in. It had also been found that jagged powder particles compact much more readily than spherical powders. To facilitate the pressing of the spherical powders they were mixed with 2 per cent paraffin by weight.

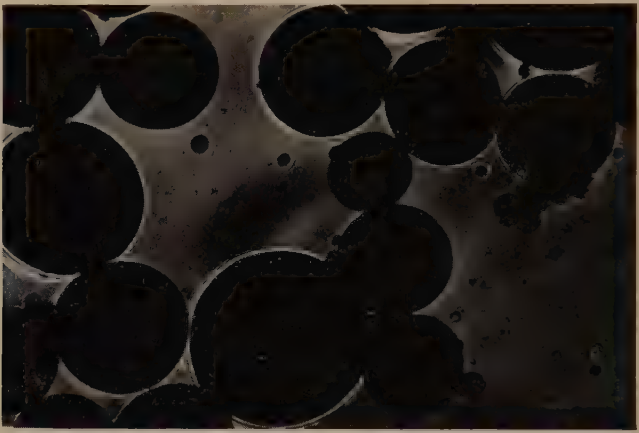


FIG. 4.—PARTICLE SHAPES OF COIN AND STERLING SILVER POWDERS. × 200. ETCHANT, DICHROMATE.

Sintering.—An attempt to sinter this material in air was unsuccessful. The compacts oxidized rather badly and would not age-harden properly. All the data presented in this paper are taken from compacts that were sintered in a hydrogen atmosphere. Two sintering temperatures were employed, one above and below the solidus (825°C. and 765°C.). No difference was noticed in the microstructure or aging characteristics of the compacts sintered at the different temperatures. The sintering time in every case was one hour. The physical properties of pressed, sintered, repressed and solution-treated compacts are shown in Table 6.

Microscopic Examination.—The photomicrograph shown in Fig. 5 is typical of the structure of these materials after pressing, sintering and repressing. The structure shows little grain growth or recrystallization. The original shape of the powder particle is very pronounced. It was believed that if grain growth and recrystallization could be fostered by proper heat-treatment, superior physical properties could be obtained.

TABLE 6.—*Physical and Electrical Properties of Coin and Sterling Silver Compacts after Various Treatments*

Treatment	Property	Coin Silver	Sterling Silver
Pressed at 10 T/sq. in.	Density, grams per c.c.	7.78	7.75
Sintered for 1 hr. at 775°C. in H_2.	Density, grams per c.c.	8.72	7.80
Repressed at 40 T/sq. in.	Density, grams per c.c.	9.81	9.65
Quenched from 775°C.	Hardness, Rock. B.	18	15
	Ultimate strength, lb. per sq. in.	29,900	39,800
	Elongation in 1 in., per cent	9.3	8.5
	Electrical conductivity, per cent I.A.C.S.	61.8	62.4
Aged 2 hr. at 280°C.	Hardness, Rock. B.	55	58
	Ultimate strength, lb. per sq. in.	39,800	41,000
	Elongation in 1 in., per cent	5.0	6.2
	Electrical conductivity, per cent I.A.C.S.	62.4	68.4

Figs. 6, 7 and 8 show compacts that were homogenized 2, 4 and 8 hr. in hydrogen at 750°C. It can be seen from this series that homogenization is probably complete after 8 hr. at this temperature.

The physical properties of the compacts prepared as follows are shown in Table 7:

1. Pressed at 10 tons per sq. inch.
2. Sintered in hydrogen for 1 hr. at 775°C.
3. Repressed at 40 tons per sq. inch.
4. Homogenized for 8 hr. at 750°C.
5. Quenched in water from 780°C.
6. Aged at 280°C. for 2 hours.

Summary.—These test results may be summarized as follows:

1. Exceptionally good physical properties can be obtained with both coin and sterling silver powders if time is allowed for sufficient recrystallization and grain growth.

TABLE 7.—*Physical Properties of Silver and Silver-alloy Compacts*

Compact	Density, Grams per C.C.	Hardness, Rockwell B		Electrical Conductivity Per Cent I.A.C.S.		Ultimate Tensile Strength, Lb. per Sq. In.	Elongation % in 1"
		Before Aging	After Aging	Before Aging	After Aging		
Coin silver...............	10.0	5	57	71.6	74.0	54,000	17.2
Sterling silver.............	9.94	10	60	71.6	79.8	55,600	12.5

2. It is possible that if the particle shape were more irregular, instead of spherical, the time necessary for recrystallization would be lowered and the percentage of voids would be reduced.

SILVER-NICKEL-COPPER COMPACTS

Silver-nickel compositions are used for electrical contacts that are often brazed to a backing. The brazing operation causes annealing of the silver-nickel contact. As sterling silver can be age-hardened at temperatures close to that at which silver brazing is accomplished, it was believed possible that a nickel-sterling silver compact might be age-hardened after brazing; thus, greater hardness and wear resistance would be imparted to the material. Experiments were undertaken in an attempt to produce age-hardenable compacts containing 85 per cent sterling silver powder and 15 per cent nickel powder. The following materials were used in the preparation of the compacts:

Sterling silver powder, 100 mesh (atomized), 92.5 per cent silver, 7.5 per cent copper.
Nickel powder, minus 325-mesh.

The compacts were pressed ½-in. diameter by ⅛ in. The pressing data are shown in Table 8.

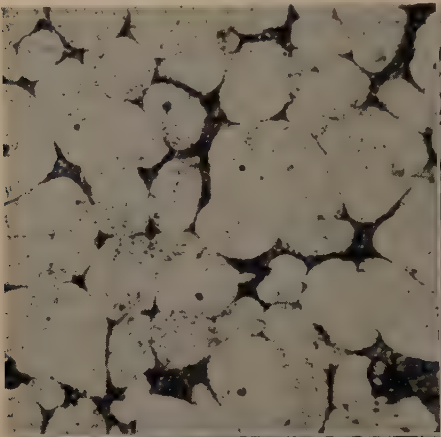
Sample 1 was fragile. The green strength of the samples increased with increasing pressure. It was necessary, however, to handle all samples with care. The large particle size and the shape of the particles (spheroid) are responsible for the low green strength.

TABLE 8.—*Pressing Data for Silver-nickel Compacts*

Sample No.	Compacting Pressure, Tons per Sq. In.	Pressed Density, Grams per C.C.
1	10	7.32
2	15	7.72
3	20	8.12
4	25	8.35

Upon sintering at 780°C. in hydrogen, the samples expanded and the density decreased. As the sintering temperature was increased, expansion decreased until the optimum temperature of 845° to 860°C. for one hour was reached. At this temperature, samples 1 and 2 sintered well and increased in density. Sample 3 remained almost unchanged in density and sample 4 decreased in density. The hardness of sterling silver compacts as previously described is 55 Rockwell B after aging at 280°C. for 2 hr. With the 85 per cent sterling silver, 15 per cent nickel compact, the maximum hardness obtainable after aging under the same conditions did not exceed 35 Rockwell F. Since copper and nickel are soluble in each other in the solid as well as liquid state, it was assumed that a portion of the copper diffused into the nickel as the temperature approached the liquidus of the copper-silver alloy. With no copper present, silver and nickel are substantially insoluble in each other. In order to check this assumption, a number of compacts containing various amounts of nickel were pressed, sintered, repressed, quenched and aged. The hardness and density data are shown in Table 9.

5



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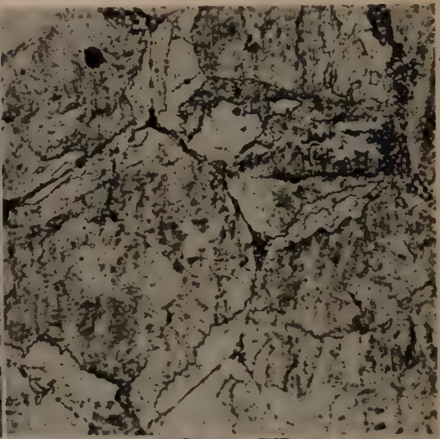

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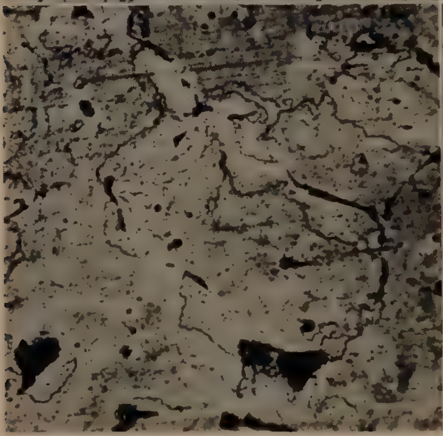

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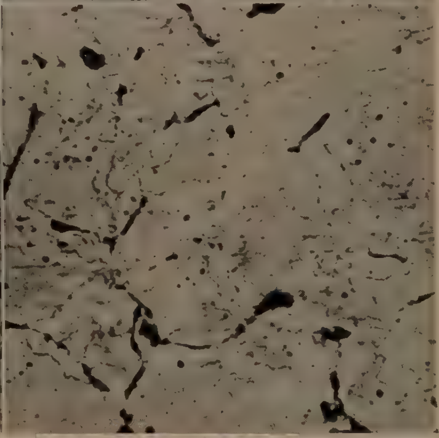


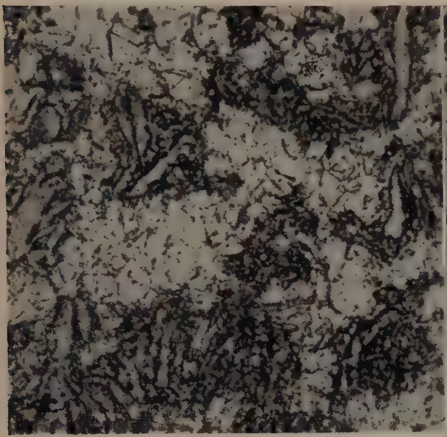
Fig. 5.—Pressed, sintered and repressed coin silver powder compact. × 200. Etchant, dichromate.

Fig. 6.—Pressed, sintered and repressed coin silver powder compact homogenized for 2 hours. × 200. Etchant: dichromate.

Fig. 7.—Pressed, sintered and repressed coin silver powder compacts homogenized for 4 hours. × 200. Etchant: dichromate.

Fig. 8.—Pressed, sintered and repressed coin silver powder compacts homogenized for 8 hours. × 200. Etchant: dichromate.

The data on hardness of the compacts after aging indicate that the highest hardness is obtained on the compacts having the lowest nickel content. The hardness decreases as the nickel content is increased, and at 15 per cent nickel reaches a minimum. With higher nickel contents, the hardness increases until at 30 per cent nickel it is essentially the same as the hardness of compacts containing 5 per cent nickel.



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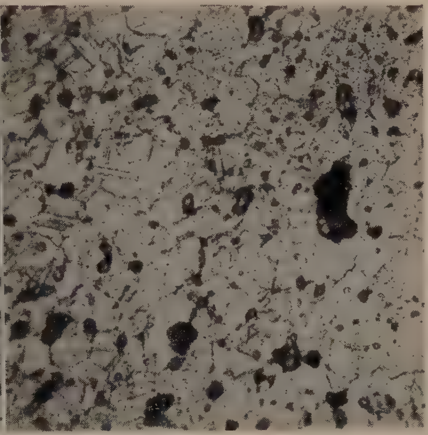

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FIG. 9.—SAMPLE CONTAINING 85 PER CENT STERLING SILVER POWDER AND 15 PER CENT NICKEL POWDER. HOMOGENIZED AND AGED. × 250.
Dark phase is nickel-copper solid solution.

FIG. 10.—DISTRIBUTION OF CADMIUM OXIDE IN SAMPLE NO. 1. × 500.
Etchant potassium dichromate.

The loss in age-hardening characteristics is due apparently to the diffusion of the copper in the nickel. The hardness in compacts containing more than 25 per cent nickel is caused by the presence of nickel particles in the compacts. Since the sintering time and temperature were kept constant for these mixtures, the amount of copper that diffused should be proportional to the concentration of the nickel, thus the compact with the least nickel content would have the most copper left, in the form of a silver-copper alloy susceptible to age-hardening.

A photomicrograph of a sample containing 85 per cent sterling silver powder and 15 per cent nickel powder is shown in Fig. 9. The dark colored phase in the matrix is a nickel-copper solid solution.

SILVER-CADMIUM OXIDE COMPACTS

Mixtures of silver and cadmium oxide have given outstanding service as heavy-

TABLE 9.—*Data on Compacts Containing Various Amounts of Nickel*[a]

Sample No.	Composition, Per Cent		Pressure, Tons per Sq. In.	Pressed Density, Grams per C.C.	Sintered Density, Grams per C.C.	Repressed Density, Grams per C.C.	Hardness after Repressing, Rockwell F	Density as Quenched, Grams per C.C.	Hardness as Quenched, Rockwell 15 T	Hardness as Aged, Rockwell F
	Sterling Silver	Nickel								
1	95	5	10	7.60	6.62	9.74	84–86	8.44	22–30	35–42
			20	8.45	7.02	9.76	83–85	8.92	34–37	45–50
2	90	10	10	7.56	6.54	9.72	85–86	8.48	32–35	24–28
			20	8.35	7.11	9.72	84–85	8.74	35–39	31–32
3	85	15	10	7.51	6.28	9.55	85–86	8.38	31–41	20–23
			20	8.23	6.82	9.59	84–86	8.52	33–38	20–24
4	80	20	10	7.26	6.06	9.47	86–87	8.28	31–38	19–24
			20	8.04	6.69	9.47	85–86	8.42	31–38	22–30
5	75	25	10	7.09	6.03	9.37	86–88	8.24	34–40	28–30
			20	7.88	6.70	9.42	86–87	8.52	41–44	37–39
6	70	30	10	6.98	5.95	9.26	87–88	8.26	40–46	33–37
			20	7.76	6.60	9.22	86–88	8.48	45–49	42–43

[a] Sintering 780° to 790°C. for one hour in hydrogen. Quenched from 780°C. after soaking for 15 minutes in hydrogen atmosphere. Aged at 300°C. for 2 hr. in air. All samples repressed at 50 tons per sq. inch.

duty contacts characterized by nonsticking properties, low contact resistance and high current carrying capacity.[1] Three compositions containing 2.5, 5 and 10 per cent cadmium oxide are compared.

TABLE 10.—*Densities of Silver-cadmium Oxide Compacts after Various Treatments*

GRAMS PER CUBIC CENTIMETER

Treatment	Sample No. 1, 2.5 % Cadmium Oxide, 97.5 % Silver	Sample No. 2, 5 % Cadmium Oxide, 95 % Silver	Sample No. 3, 10 % Cadmium Oxide, 90 % Silver
1. Pressed at 10 to 15 tons per sq. in......	7.85	7.72	7.50
2. Sintered 1 hr. at 800°C. in air........	8.43	8.19	7.8
3. Repressed at 50 tons per sq. in..........	10.1	9.99	9.8

The density after pressing, sintering and repressing, decreases with increasing contents of cadmium oxide (see Table 10). The electrical and physical properties of the compact in the hard and annealed condition are shown in Table 11. Of particular interest are the high electrical conductivity values, permitting the use of these materials for continuously carrying high currents without excessive rise of temperature.

A typical photomicrograph is represented in Fig. 10, showing the general distribution of cadmium oxide in sample 1. The material identified as sample 1 is ductile and can be produced in wire or strip form, from which contacts or other parts may be headed or blanked.

A comparison with silver-cadmium alloys indicates that the silver-cadmium oxide materials can be produced with considerably higher electrical conductivity values. A series of alloys was prepared containing 3.02 per cent cadmium, 5.68 per cent cadmium and 10.84 per cent cadmium, respectively. The respective conductivities of these solid solution alloys are given in Table 12.

TABLE 11.—*Conditions of Silver-cadmium Compacts after Annealing*

Material	Electrical Conductivity, Per Cent I.A.C.S.	Hardness, Rockwell F	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 1 Inch
Sample No. 1, full hard......	88.7	74	25,208	1.56
Sample No. 1, annealed ½ hr. at 600°C.....	94.9	18	18,017	16.78
Sample No. 2, full hard......	83.6	76	25,068	1.56
Sample No. 2, annealed ½ hr. at 600°C......	93.5	30	17,014	8.57
Sample No. 3, full hard......	69	81	26,000	0
Sample No. 3, annealed ½ hr. at 600°C......	80	40	17,000	4

TABLE 12.—*Conductivities of Solid Solution Alloys*

Material	Electrical Conductivity, Cold-worked, Per Cent I.A.C.S.	Electrical Conductivity after Annealing, ½ Hr. at 650°C., Per Cent I.A.C.S.
3.02 per cent Cd, bal. Ag...	67	72.5
5.68 per cent Cd, bal. Ag...	52.6	59.2
10.84 per cent Cd, bal. Ag...	39.25	44.2

Silver-cadmium-oxide compacts have been prepared with various percentages of cadmium oxide, from very low up to preponderant amounts. The percentage of cadmium oxide depends on the specific contact application. The material represented by sample 3 is used extensively in heavy-duty relays and provides in such applications a material that will maintain an unusually low contact resistance for long periods of time and will withstand very heavy overloads without welding or sticking.

CONCLUSIONS

Silver-base powder metallurgical products are used in the electrical industry in highly specialized applications such as structural parts, make and break contacts and sliding contacts.

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[1] F. R. Hensel: U.S. Patent 2145690.

It should be mentioned that, in addition to the standard methods described in this paper, special procedures have been developed for the manufacture of materials with high arc-erosion resistance and low contact resistance (Elkonite process). The characteristics of such materials have been previously described.[1]

SUMMARY

1. Pressing at temperatures ranging from 25° to 450°C. has little effect on the density and hardness of fine silver compacts.
2. The density of fine silver compacts pressed at 12.5, 25, and 50 tons per sq. in. and sintered at 880°C. in air was the highest on compacts pressed at 12 tons per sq. in. The higher density was retained throughout subsequent repressing and resintering operations.
3. Silver compacts sintered in air have higher physical and electrical properties than those sintered in hydrogen.
4. Coin and sterling silver compacts fabricated from alloy powders and sintered in hydrogen exhibit mechanical and electrical properties similar to those of the wrought alloys. Such compacts respond to precipitation-hardening treatments to a high degree.
5. Increasing additions of nickel (5 to 30 per cent) to sterling silver compacts progressively decreases their susceptibility to precipitation-hardening.
6. By replacing cadmium with cadmium oxide in silver compacts, materials of high electrical conductivity are obtained, which have applications as electrical contacts.

ACKNOWLEDGMENTS

The authors wish to acknowledge the valuable assistance rendered by Messrs. E. F. Swazy, F. H. Vandenburgh and C. H. Bean, of the Metallurgical Engineering Department of the P. R. Mallory and Co., Inc., in carrying out the experimental work.

DISCUSSION

(F. N. Rhines presiding)

P. R. KALISCHER.*—I should like to amplify a little one of the points made by Dr. Hensel, and rather violently disagree with him at the same time. He brought out the point that when the higher forming pressures are used on the green compacts there is a marked decrease in the density as sintered. We found that to be true and, of course, many of you notice that that is true with copper compacts also. But, in my opinion at least, it is not true that the expansion is due to entrapped air. We have vacuum-pressed both silver and copper compacts and obtained almost exactly the same numerical expansion as we secured by pressing in air. The powder, however, that is vacuum-annealed does show a slight decrease in expansion on sintering, but almost the entire increase on expansion can be overcome by very slow rates of heating. And it is our opinion that a majority of the expansion is due to dissolved oxygen in the discrete metal particles themselves rather than to entrapped gases.

Another interesting observation that we have made is that often with silver or copper compacts it is desirable to silver solder or braze the compact into some part of a piece of equipment after completing powder metallurgical operations on it. If such a compact is sintered and coined, say a silver compact, given an initial forming pressure of 10 to 15 tons per square inch, and sintered, there is an adequate amount of shrinkage and it can be coined at about 50 or 60 tons per square inch and bring up the density nearly to theoretical. If, then, that compact is silver-soldered into some part of a fixture or a machine, it will expand very beautifully, and the only way that this can be overcome, as far as we know, has been to reanneal after the coining operation at a temperature higher than is to be used in any subsequent operation. In that way, a density very nearly theoretical can be achieved, but the coining operation cannot be carried to the excessively high pressures or expansion and bubbling of the compact will occur again.

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[1] F. R. Hensel, E. I. Larsen and E. F. Swazy: Tungsten-copper alloys for electrical contacts. *Metals and Alloys* (1941) **13**, 577–583.

* Westinghouse Electric and Manufacturing Co., Pittsburgh, Pa.

Some Properties of Sintered and Hot-pressed Copper-tin Powder Compacts

By Claus G. Goetzel,* Member A.I.M.E.

(New York Meeting, February 1944)

Until recently porous bronzes have found many applications for self-lubricating bearings in the automotive, electrical, household appliance and general machine industries. The bulk of an annual production of several million pounds of copper powder had gone into the manufacture of these articles, of which by now more than a billion are in service. However, the war has brought severe curtailment of these bearings because of the scarcity of the two main constituents, copper and tin. The development of substitute materials of equal or superior properties has led to a large-scale replacement by products made from iron powder.

In spite of the diminished interest in powdered copper-tin alloys caused by this trend, it was believed worth while to investigate some mechanical properties of these materials as a reference base for substitutes. In addition, experiments using the hot-press method were incorporated to investigate possibilities of saving vital equipment or opening new fields of applications.

It must be assumed that by this time the powder metallurgy process of making porous bronzes, a development that found its first industrial applications more than 10 years ago, is well known in engineering. The patent literature and bibliography is voluminous, most publications referring to porous, self-lubricating bronzes, containing about 10 per cent tin and 1 to 5 per cent graphite, with porosities in the range of 25 to 35 per cent.[1-7] The excellent antifriction properties of these bearings, caused by the uniform impregnation with oil, are dependent on the interconnection of the pores and the uniform distribution of the graphite inclusions. The sintering mechanism of porous bronze, with its structural changes during the transformation of the metal powder into the sintered bearing has been shown in colored photomicrographs by Hall.[8] Diffusion between copper and tin was found to begin within one minute, when tin-rich transitory phases were formed. After 25 min. a homogeneous matrix of alpha was reached for an alloy containing 9.5 per cent tin and 6 per cent graphite.

Price, Williams and Garrand,[9] studying certain metal powder combinations in which sintering is accompanied by the cementing action of a liquid phase, including a 90-10 bronze sintered at 925°C., have found that if the treatment is carried out within the liquidus and solidus temperature range of the system, a peculiar process of alternate solution and precipitation occurs. The particles of the major solid constituent are dissolved in the minor liquid phase, but thereafter are reprecipitated on certain nuclei, which develop into large grains, usually rounded.

Manuscript received at the office of the Institute April 4, 1942; revised June 18, 1943. Listed as T. P. 1639.

* Assistant Director of Research, American Electro Metal Corporation, Yonkers, N. Y.

[1] References are at the end of the paper.

Sintering almost always is accompanied by volumetric changes. The main causes of the growth are release of stress originating from the briquetting operation and evolution of gases during sintering caused by reactions during alloying, or by gases that had been absorbed by the powder during storage or entrapped during the high-pressure molding (air). Shrinkage is effected by atomic movements, alloying, creep, and surface tension forces. All these effects are concurrent, and the extent of the volume changes is affected by the type, distribution of particle size and total surface area of each powder constituent, and by reactions between them. Conditions prevailing during molding and sintering also are influential, such as the evaporation of volatile lubricants, usually mixed with the powders to facilitate cold-pressing.

The volumetric changes have been brought under control for many industrial applications by improved production methods and the introduction of a final sizing operation. Although the extent of these changes is not as large in bronzes as for sintered brasses,[10] the control of shrinkage on the manufacturing process is still largely empirical, constituting one of the most difficult problems of the entire process.[11]

The changes in volume during sintering are influenced by the raw material, and control efforts have led to the investigation of prealloyed powders, in which many of the reactions causing these volumetric changes can take place in the powdery mass during the preliminary treatment. Prealloying the powders by sintering has led to considerable improvement in brass. This is confirmed by Drapeau and Larssen and Vandenburgh for bronzes.[10] On the other hand, Jones[12] reports little success with alloy powders, which gave compacts of inferior strength.

The hot-press method offers an ideal approach to the control of the dimensions of the powder compacts, as the material remains confined to a definite space during the high-temperature treatment. At the same time, materials of high density and physical properties can be developed by making use of the increased plasticity of the powder particles at elevated temperatures. The method, industrially developed in the case of cemented carbides, has been used in a number of investigations of single metal powders.[13–15] The only work on hot-pressing of bronzes so far known has been done by Jones in England, who has experimented with binary tin bronzes made from mixed constituents and from atomized alloys. For these experiments, a setup has been used that must be considered as preliminary in the development of industrial hot-press equipment. In spite of the fact that no controlled atmospheres were employed for the high-temperature work, physical properties of remarkable order were obtained, with tensile values above 40,000 lb. per sq. in. and elongations up to 75 per cent. These encouraging results indicated a commercial field for solid bearings in the near future and justified further study of the subject.

EXPERIMENTAL PROCEDURE AND RESULTS

Material.—Table 1 gives details of the initial metal powders used. While the

TABLE 1.—*Properties of Electrolytic Copper and Tin Powders* (*Purity* 99.5+ *Per Cent*)

Analysis and Particle Size	Copper, Per Cent	Tin, Per Cent
Screen Analysis (U. S. Standard), Mesh		
−100+140	6	nil
−140+200	19	nil
−200+230	3	nil
−230+325	24	nil
−325	48	100
Particle Size Distribution,[a] Microns		
0– 5	nil	29
5– 10	2	33
10– 20	15	27
20– 30	14	7
30– 40	12	3
40– 50	10	1
50– 75	23	nil
75–100	19	nil
+100	5	nil
Apparent density, grams per c.c.	2.5	2.3

[a] As determined by microscopic count.

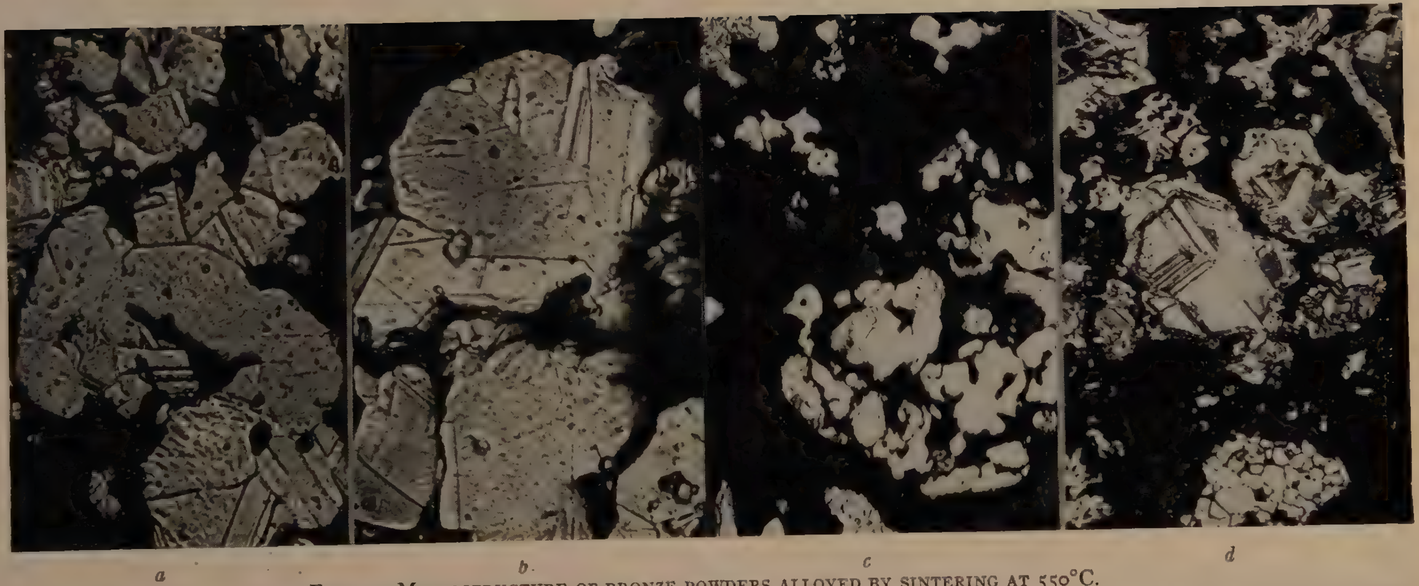

FIG. 1.—MICROSTRUCTURE OF BRONZE POWDERS ALLOYED BY SINTERING AT 550°C.

a. 95-5 Cu-Sn. × 1000. Etched with 50 per cent solution of HNO_3 in alcohol. Homogeneous alpha solid solution in the great majority of particles. Pure copper and isolated specks of delta occasionally present.

b. 90-10 Cu-Sn. × 1000. Etched with 50 per cent solution of HNO_3 in alcohol. Alpha alone present in most particles. Small areas of pure copper, delta, eutectoid next to alpha found in some particles.

c. 85-15. Cu-Sn × 500. Etched with 1:1:4 $FeCl_3$, HCl and H_2O. Main constituents are alpha and eutectoid. Delta alone present in a few particles. No areas of pure copper.

d. 80-20 Cu-Sn. × 500. Etched with 1:1:4 $FeCl_3$, HCl and H_2O. Alpha still predominant, sharing most particles with delta and eutectoid. Delta frequently forming a border around alpha. Occasionally entire particles consist of aggregates of delta crystallites (see bottom particle).

electrolytic copper powder was of commercial grade (minus 100 mesh), the tin powder used was extremely fine (minus 325 mesh), to assure rapid diffusion during the prealloying treatment.

Powder mixes corresponding to 95-5, 90-10, 85-15 and 80-20 Cu-Sn were prepared by tumbling dry for 24 hr. followed by cleaning at 275°C. for 1 hr. in dessicated hydrogen and for another hour in vacuum and subsequent cooling in vacuum. Part of each powder mix was sintered for 1 hr. at 550°C. in a tubular muffle furnace for prealloying. A second hour of heat-treatment in vacuum at the same temperature was followed by furnace cooling. The alloy powders were pulverized in a mortar to pass a 100-mesh sieve. Fig. 1, showing photomicrographs of the structure of representative powder particles of the four compositions, gives evidence of the success of the alloying treatment. In the 95-5 and 95-10 compositions the particles consisted substantially of alpha with very few specks of delta or eutectoid noticeable. Naturally, with higher tin content eutectoid and delta areas became more apparent, but even the 80-20 alloy powder contained a majority of particles with alpha as predominant phase.

Procedure.—The techniques used in preparing the powder compacts have been described elsewhere in detail,[15] but minor variations in procedure suggest a brief description of methods and apparatus.

Part of the powder was taken for briquetting at room temperature followed by sintering at 800°C. for 1 hr. in hydrogen in a tubular resistance furnace and subsequent furnace cooling. Cylinders approximately 9⁄16 in. in diameter and ½ in. long were compacted at pressures ranging from 5 to 50 tons per sq. in. by pressing from two opposite directions.

To facilitate hot-pressing, the powders were premolded cold in the same manner but at lower pressures, ranging from 2 tons per sq. in. for mixed powders to 8 tons per sq. in. for the tin-rich alloyed powders. The cylinders were dropped into the slightly oversized cavity of a preheated die. This die was built from high-speed steel in such manner as to permit working temperatures up to 600°C., continuous pressures up to 50 tons per sq. in., introduction of a reducing atmosphere into the die cavity and cooling channel through a circumferential gas chamber, and water-quenching of the hot-pressed compacts. Heat was supplied by an electric resistance furnace surrounding the die and temperatures were kept constant within 10°C., the hot junction of the thermocouple placed as close as possible to the specimen. The work cycle provided for a 5-min. preheating time before application of pressure, in order to assure uniform temperature. Pressure was applied for one minute, and the total operation consumed less than 8 min., including quenching. Hot-pressing was carried out at two temperatures, at 300°C. just above the melting point of tin and at 500°C. close to the maximum temperature limit for the high hot strength of the steel.

Testing.—The highly specialized equipment available for the hot-press experiments permitted the production of only small cylindrical compacts. For this reason testing of physical properties was limited to the determination of density, hardness and compressive properties.

The density of the compacts was determined by pycnometric and weight-volume measurements, and hardness was tested on the Rockwell E scale and then converted into Brinell equivalents. Standard specifications for compression tests of bearing metals[17] were followed by keeping the dimensions of the cylinders to the ratio of $h = 0.9d$, although the cylinders did not correspond to the standard "short" specimen. All other regulations of the A.S.T.M. standards were followed. In addition to the determination of the maximum compressive strength, obtained from the maximum load that each specimen could sustain, deformation under such condition was measured by percentage reduction in length (compression) and increase in area. In order to have a means of comparison with common bearing metals, the compressive strength was also determined for a reduction in length of 0.1 in. (compression of 0.1 in.) wherever the material was ductile enough to permit the reduction of 20 per cent in length.

Results.—All sintered bronze compacts underwent only negligible changes in weight during heat-treatment, with maximum weight gains of 0.29 per cent and maximum weight losses of 0.67 per cent. Volumetric changes, on the other hand, were considerable, as shown by the data of Table 2. For low tin compositions, alloy powder compacts shrink less than mixed powder compacts in the low-pressure range, but this is reversed for the tin-rich compositions, for which shrinkage figures above 30 per cent by volume were observed for very lightly briquetted material.

TABLE 2.—*Percentage Volume Changes of Bronzes Sintered at 800°C. for One Hour*

Raw Material and Composition	Compacting Pressure, Tons per Square Inch				
	5	10	15	25	50
95-5 Cu-Sn					
Mixed powder.	−23.6	−20.8	−16.4	−8.4	+0.6
Alloy powder. .	−12.8	− 8.8	− 5.8	−3.0	−0.4
90-10 Cu-Sn					
Mixed powder.	−22.8	−21.4	−15.1	−4.4	+0.8
Alloy powder. .	−14.4	− 9.9	− 6.9	−4.9	−2.7
85-15 Cu-Sn					
Mixed powder.	−33.9	−23.4	−15.2	−6.2	+1.6
Alloy powder. .	−30.1	−21.3	−14.6	−6.9	−2.6
80-20 Cu-Sn					
Mixed powder.	−30.5	−14.6	− 5.1	+0.5	+2.9
Alloy powder. .	−29.7	−19.3	−14.7	−7.9	−2.3

The results of microscopic inspection of the various structures are indicated by the photomicrographs of Figs. 2 to 5. As expected, prealloying of the powders promoted increased homogenization in all hot-pressed samples, but it was much less effective in sintered specimens, with virtually no effects in the 95-5 and 90-10 compositions. Other features of the microstructure are decreased porosity with rising pressures and grain growth and normalization of the structure during sintering. For hot-pressed material, greatly increased densification is coupled with only partial recrystallization and substantial retention of a structure of closely agglomerated powder particles.

The effects of material, composition, pressure and temperature on density, hardness and compressive strength are indicated in the representative diagrams Figs. 6 to 9. These properties increase with rising molding pressure, both for sintered and hot-pressed materials. Specimens hot-pressed at 300°C. show lowest physical properties, with the sole exception of the hardness of cylinders pressed at 50 tons per sq. in. Specimens hot-pressed at 500°C. reach theoretical densities, high hardness and compressive properties comparable with normal alloys of similar composition. The sintered alloys have intermediate density and compressive-strength values and, of course, lowest values for hardness. The kind of initial material has the following effects: Density of the sintered compacts is improved by prealloying and the opposite is found, in most instances, for hot-pressed compacts; specimens of the tin-rich compositions pressed at 500°C. at high pressures are the only exception. Hardness values show a similar trend, except that low-tin prealloyed powders form harder compacts when hot-pressed. The use of alloy powders leads to improved compressive properties in all compositions made by both methods.

DISCUSSION OF EXPERIMENTAL RESULTS

Weight and Volume Changes.—The insignificant weight changes during sintering substantiate the purity of the raw materials employed. The extent of the volumetric changes, on the other hand, is considerable, and the following conclusions can be drawn: (1) shrinkage is predominant; (2) shrinkage is generally decreasing with increasing initial pressure (higher "green" density); (3) shrinkage figures are the highest for materials of the 85-15 composition; lower

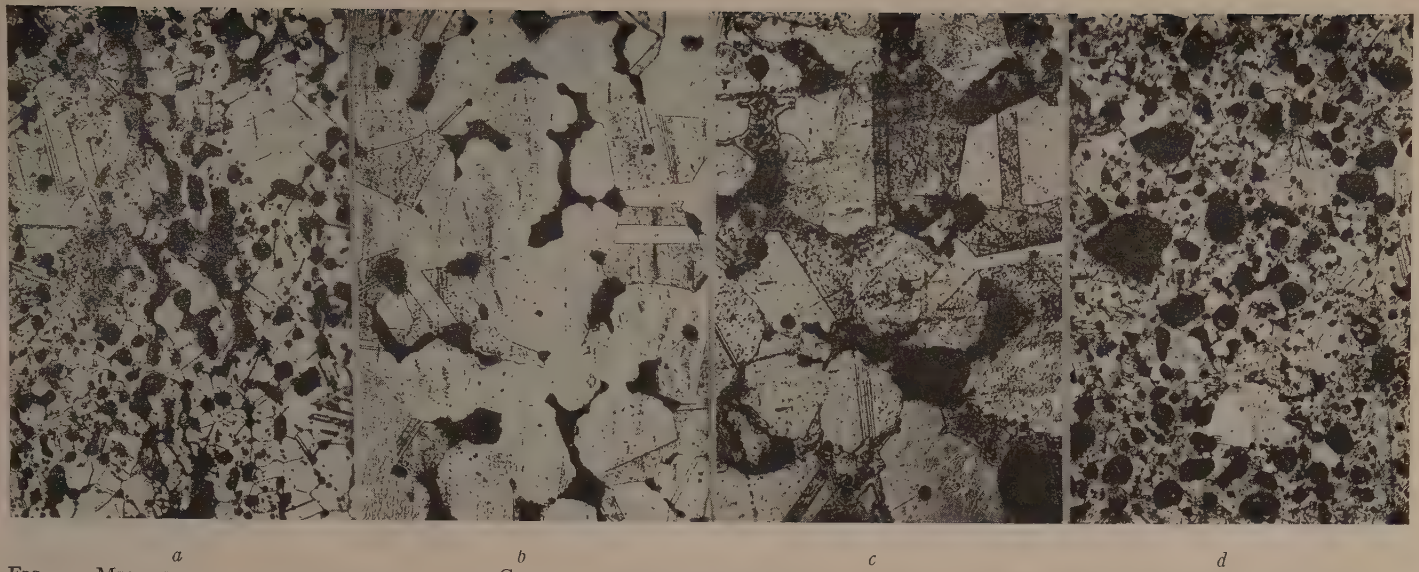

FIG. 2.—MICROSTRUCTURE OF SINTERED BRONZES. COMPACTS PRESSED FROM MIXED POWDERS AT 50 TONS PER SQUARE INCH AND SINTERED AT 800°C. FOR ONE HOUR.

a. 95-5 Cu-Sn. × 200. Etched with 1:1:1 NH_4OH, H_2O_2, H_2O. Fine-grained alpha solid solution. Isolated small areas of eutectoid found occasionally. Excessive porosity.

b. 90-10 Cu-Sn. × 200. Etched with 10 per cent aq. soln. of $(NH_4)_2S_2O_8$. Substantially homogeneous solid solution. Grain size larger and uniform. Eutectoid areas rare. Considerable porosity.

c. 85-15 Cu-Sn. × 200. Etched with 10 per cent aq. soln. of $(NH_4)_2S_2O_8$. Solid solution predominant, its grain size similarly large, well-formed grain boundaries. Increased amounts of eutectoid. Isolated areas of delta evenly dispersed throughout alpha matrix. Considerable porosity.

d. 80-20 Cu-Sn. × 200. Etched with 10 per cent aq. soln. of $(NH_4)_2S_2O_8$. Structure rather uniform consisting of fine-grained alpha and eutectoid, both present in about equal amounts. Excessive porosity.

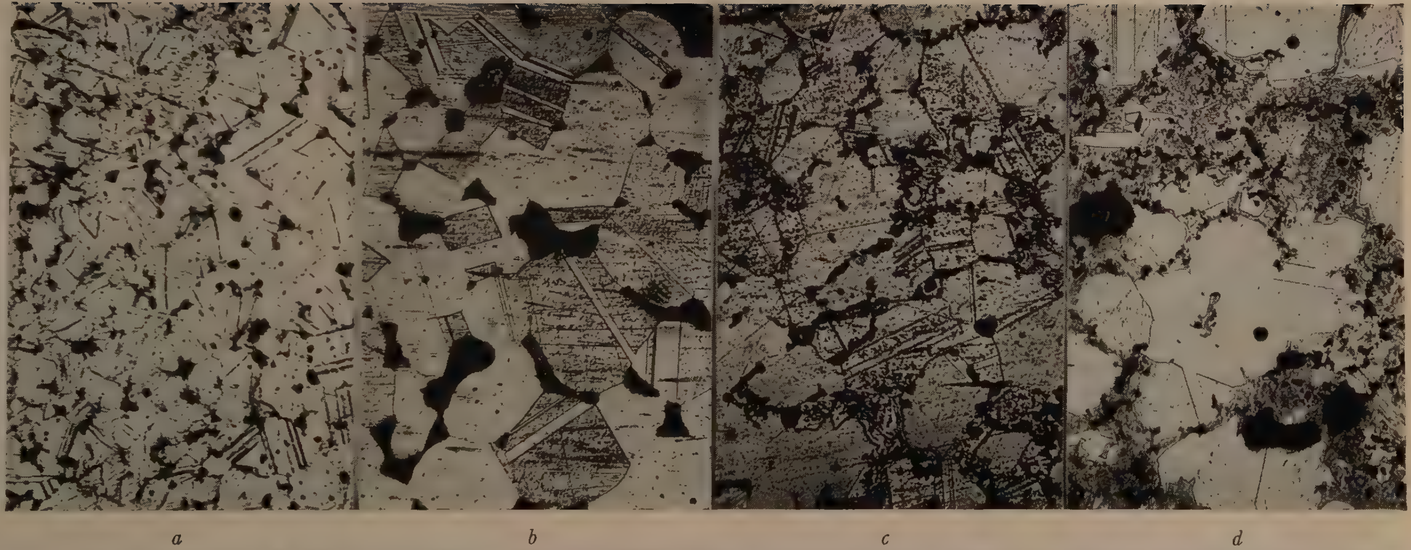

FIG. 3.—MICROSTRUCTURE OF SINTERED BRONZES. COMPACTS PRESSED FROM ALLOY POWDERS AT 50 TONS PER SQUARE INCH AND SINTERED AT 800°C. FOR ONE HOUR.

a. 95-5 Cu-Sn. × 200. Etched with 1:1:1 NH_4OH, H_2O_2, H_2O. Structure homogeneous. Fine-grained alpha found throughout, with little evidence of eutectoid. Moderate porosity.

b. 90-10 Cu-Sn. × 200. Etched with 10 per cent aq. soln. of $(NH_4)_2S_2O_8$. Structure completely homogeneous. No other constituents than alpha. Grain size larger and uniform. Moderate porosity.

c. 85-15 Cu-Sn. × 200. Etched with 10 per cent aq. soln. of $(NH_4)_2S_2O_8$. Alpha matrix and uniform network of eutectoid. No delta. Slight porosity.

d. 80-20 Cu-Sn. × 200. Etched with 10 per cent aq. soln. of $(NH_4)_2S_2O_8$. Structure uniformly consisting of alpha and eutectoid network, both constituents present in about equal amounts. Moderate porosity.

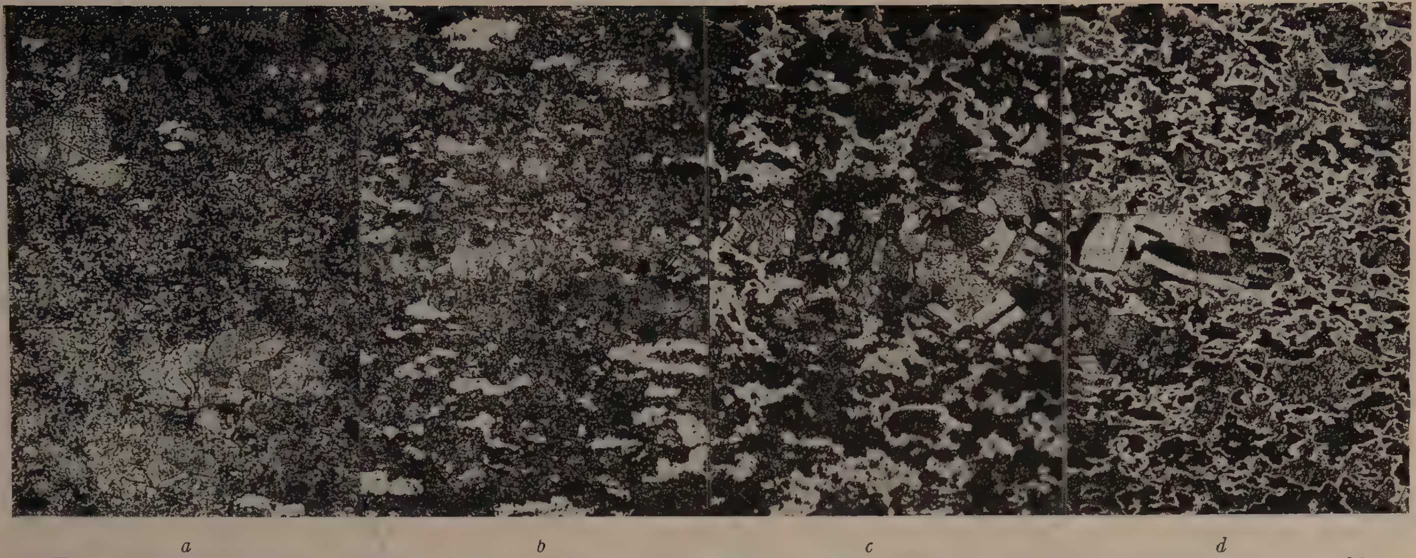

FIG. 4.—MICROSTRUCTURE OF HOT-PRESSED BRONZES. COMPACTS PRESSED FROM MIXED POWDERS AT 50 TONS PER SQUARE INCH AND 500°C.

a. 95-5 Cu-Sn. × 200. Etched with 5:10:100 $FeCl_3$, HCl, H_2O. Structure very dense, but heterogeneous. Particles agglomerated, containing recrystallized alpha and frequent well-dispersed delta areas. Concentration gradients in solid solution regions. Entire particles still consisting of copper-rich areas with their original nodular structure discernable.

b. 90-10 Cu-Sn. × 200. Etched with 5:10:100 $FeCl_3$, HCl, H_2O. Structure very dense and heterogeneous, consisting of three constituents. Partly recrystallized alpha in a majority of particles. Delta areas are abundant, frequently being pressed into plates in planes perpendicular to the axis of pressure. Occasional copper-rich particles, their original nodular structure often retained.

c. 85-15 Cu-Sn. × 200. Etched with 5:10:100 $FeCl_3$, HCl, H_2O. Structure again very dense and heterogeneous. A matrix of alpha-containing particles and a network of delta are predominant. Concentration gradients in most alpha particles. Some nodular copper-rich particles still present. Eutectoid and tin-rich transitory phases also recognizable.

d. 80-20 Cu-Sn. × 200. Etched with 5:10:100 $FeCl_3$, HCl, H_2O. Structure again very dense and heterogeneous. Agglomerate of alpha-containing particles. Concentration gradients still evident. Delta network pronounced. Tin-rich transitory phases and eutectoid are even more apparent.

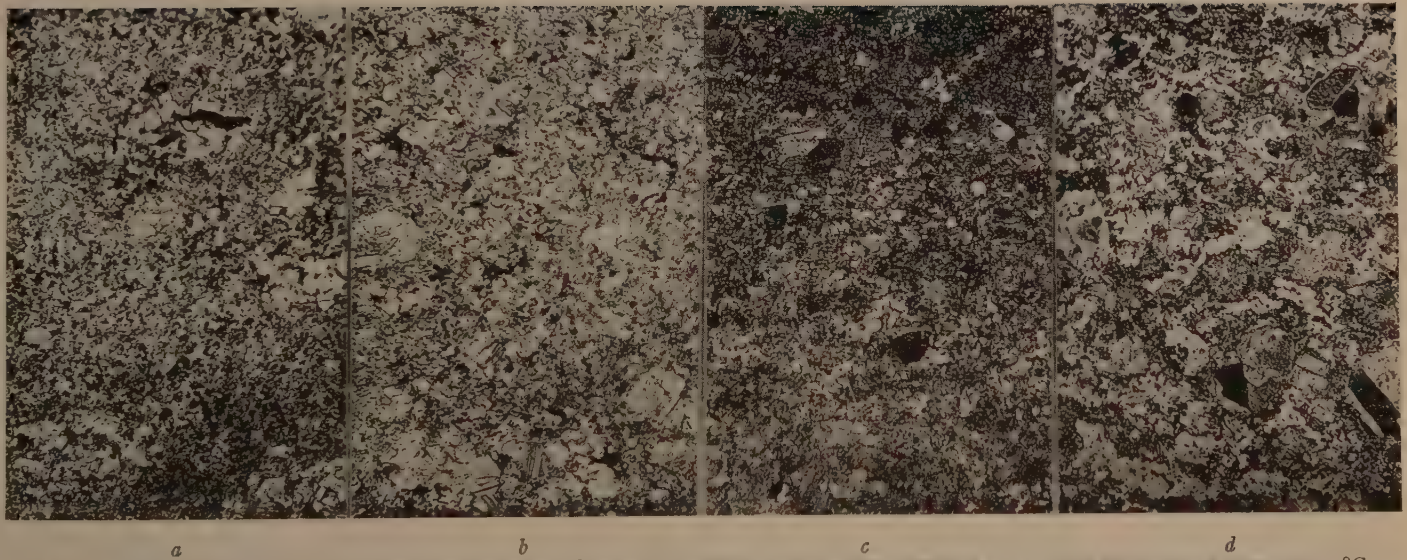

FIG. 5.—MICROSTRUCTURE OF HOT-PRESSED BRONZES. COMPACTS PRESSED FROM ALLOY POWDERS AT 50 TONS PER SQUARE INCH AT 500°C.

a. 95-5 Cu-Sn. × 200. Etched with 5:10:100 $FeCl_3$, HCl, H_2O. Structure very dense, rather homogeneous. Concentration gradients in alpha only rarely detectable. Small areas of delta occasionally visible.

b. 90-10 Cu-Sn. × 200. Etched with 10 per cent aq. soln. of $(NH_4)_2S_2O_8$. Structure very dense, rather homogeneous. Fine-grained alpha matrix predominant, with original particle boundaries almost completely dissolved. Delta inclusions very rare.

c. 85-15 Cu-Sn. × 200. Etched with 5:10:100 $FeCl_3$, HCl, H_2O. Structure dense, fairly uniform, consisting of a matrix of fine-grained homogeneous alpha and of evenly distributed delta areas.

d. 80-20 Cu-Sn. × 200. Etched with 5:10:100 $FeCl_3$, HCl, H_2O. Structure dense, fairly uniform. Rather large alpha grains embedded in a network of delta. Infrequent areas of eutectoid.

tin compositions show less varied volume changes, and compacts of the 80-20 composition exhibit a marked trend toward growth; (4) prealloyed powders cut shrinkage figures in half for the low-pressed low-tin alloys and cause little shrinkage for the same compositions molded at high pressures, but they cause marked shrinkage in the tin-rich compositions.

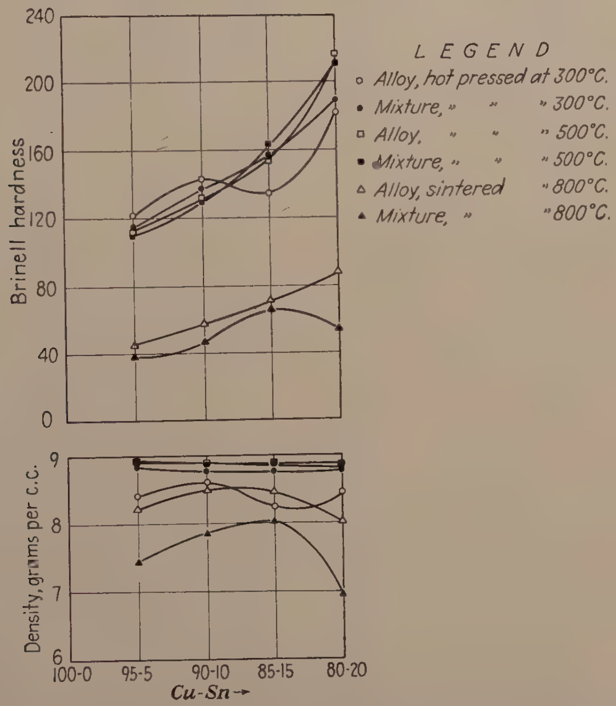

FIG. 6.—DENSITY AND HARDNESS VS. COMPOSITION FOR COMPACTS PRESSED AT 50 TONS PER SQUARE INCH.

Volumetric and weight changes during hot-pressing have been found of such small order that their recording has only academic value.

Density.—The density of the cold-pressed compact is a determining factor for the final value, often superseding the shrinkage effects during sintering. However, the tendency of powder particles of subsieve size to promote excessive shrinkage and densification must be taken into account and is the main reason for certain restrictions in the amount of fines permitted in the powders used in the manufacture of porous bearings. In this investigation it was found that: (1) density increases with molding pressure, regardless of composition, both for sintered and hot-pressed materials; (2) maxima not exceeding 95 per cent of the theoretical value are reached in sintered compacts for the range of initial pressures used; (3) compacts of similar density can be reached by hot-pressing at 500°C. at approximately one tenth of the pressure; (4) the compacts hot-pressed at lower temperatures approach theoretical density values at increased pressure, while compacts pressed at 500°C. reach the theoretical limit at low pressure; (5) in sintered compacts prealloyed powders yield higher densities only if briquetted above 15 tons per sq. in.; (6) hot-pressed compacts are denser when made from the powder mixtures, especially for the materials pressed at low temperatures, indicating increased plasticity and effective cementing caused by the liquid tin or tin-rich phases.

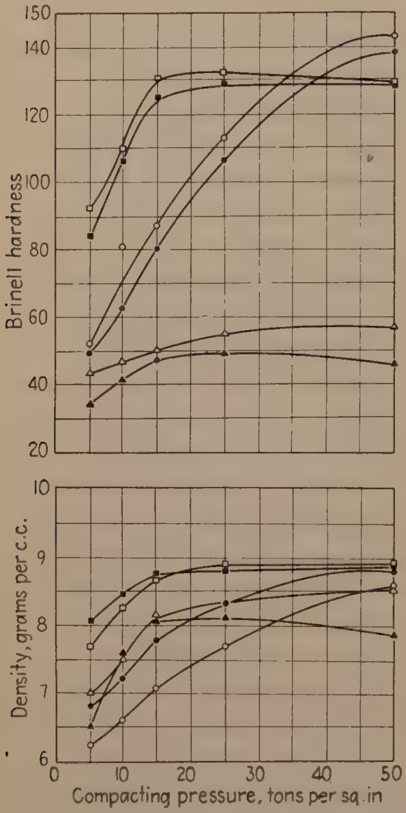

FIG. 7.—DENSITY AND HARDNESS VS. PRESSURE FOR 90-10 BRONZE.

Hardness.—The very low hardness values of the sintered bronzes can be explained by their porosity. The hardness of the hot-pressed compacts, on the other hand, is improved not only by the increased density but also by severe straining of the particles when pressed at high pressures below the recovery temperature range. It was found that: (1) bronzes pressed between 5 and 50 tons per sq. in. and sintered at 800°C. have only about half the hardness of solid metals of the same composition; (2) with increasing molding pressure, maxima are obtained at about 25 tons per sq. in., (3) hot-pressed compacts are generally much harder, in many cases comparing with severely work-hardened bronzes; (4) compacts hot pressed at 500°C., displaying a hardness comparable with the best figures obtained in the sintered metal, require only about one tenth of the cold molding pressure; (5) the hardness of hot-pressed bronze compacts increases with rising molding pressure, reaching maximum values for compacts pressed at 500°C. and 25 tons per sq. in.; (6) hardness of compacts hot-pressed at 300°C. is lower, owing to lower density, only the more ductile low-tin compositions yielding higher hardness values when severely strained at 50 tons per sq. in. pressure; (7) the expected increase in hardness with rising tin content is apparent both for sintered and hot-pressed materials.

Compressive Properties.—The results of the compression tests permit the following observations: (1) Bronzes sintered at 800°C. stand up well under compression, comparing favorably with the bulk metal; strength and ductility figures increase with rising initial pressure, and reach maxima at 15 to 25 tons per sq. in.; (2) in hot pressed compacts these properties can be reached only if the material is pressed at or above 500°C.; (3) in hot-pressed compacts, strength and ductility increase with rising molding pressures to maxima above 25 tons per sq. in.; (4) all compacts hot-pressed at 300°C. are naturally poor in strength and ductility; (5) the properties can be improved if the compacts are of sufficiently uniform structure, such as obtained by prealloying; in sintered bronzes, this is most evident for the low-tin alloys; it is less apparent for the tin-rich compositions; (6) the effect of composition on the compressive properties is as expected: with rising tin content maximum values are reached for the 90-10 composition followed by a substantial drop in strength and ductility for the alloys higher in tin.

Structure.—Sintered bronzes, especially of the lower tin content, display a grain structure resembling ordinary metal. Fine grain size and an evenly distributed network of microscopic pores constitute the main difference. After heat-treatment for one hour at 800°C., homogeneous solid solutions are obtained with the 95-5 and 90-10 compositions. Abundant porosity in the compacts molded at low pressures impedes diffusion in these materials. Compacts hot-pressed at 300°C. from mixed powders consist merely of compressed powder particles with little evidence of diffusion. The size and amount of pores decreases with rising pressures, but complete densification is obtained only at 500°C.; then the material still consists of an agglomerate of the initial powder particles with recrystallized alpha recognizable. Materials prepared from prealloyed powders display a slightly more homogeneous structure. Compacts hot-pressed from the powder mixtures with higher tin contents have a very heterogeneous structure, with transitory tin-rich phases present next to eutectoid, delta and alpha regions. Even materials of the 95-5 composition contain some of these tin-rich phases. Solid solution areas often show concentration gradients, and entire particles still consist of copper-rich areas with the initial nodular structure originating from the electrolysis of the copper. The obscurity of the grain structure of these hot-pressed materials is understandable in view of the method of their preparation.

Materials.—In comparing mixed powders with prealloyed powders, certain advantages in using alloy powders are apparent for the hot-press method. Considerable improvements in hardness, strength and ductility are obtained through increased homogenization of the alloys. Prealloying of the powders, however, increases the rigidity of the individual particles, thus causing increased resistance to compression and slightly less dense compacts. The

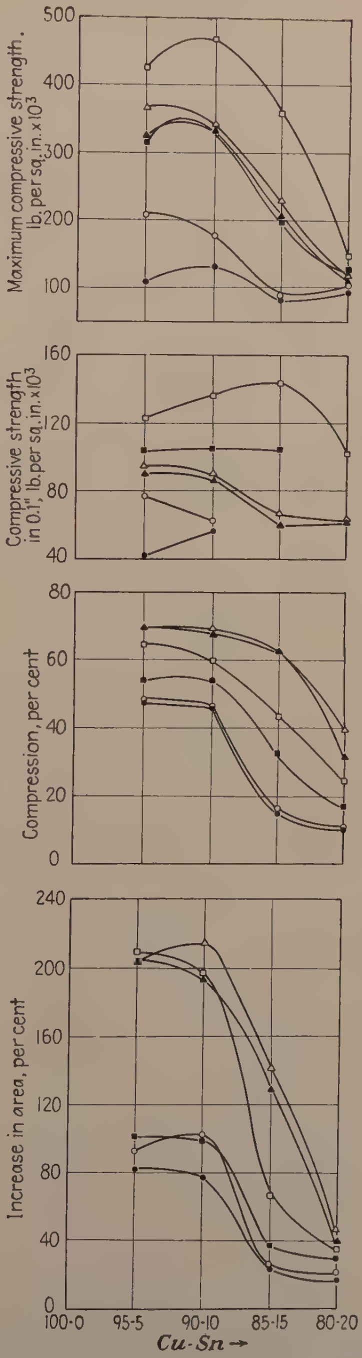

FIG. 8.—COMPRESSIVE PROPERTIES VS. COMPOSITION FOR COMPACTS PRESSED AT 50 TONS PER SQUARE INCH.

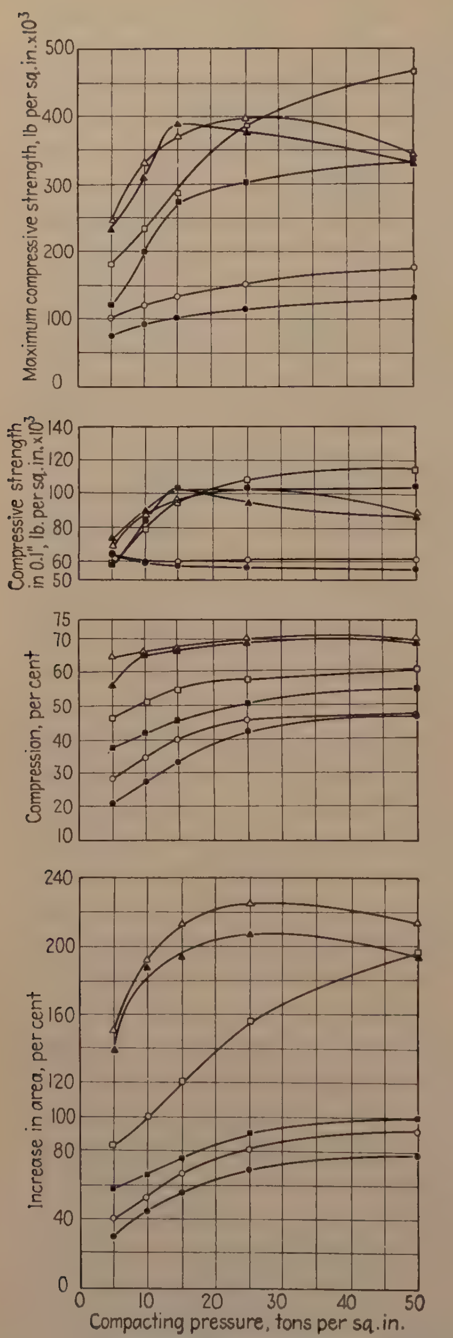

FIG. 9.—COMPRESSIVE PROPERTIES VS. PRESSURE FOR 90-10 BRONZE.

greater resistance to compression is overcome at elevated temperatures, and complete consolidation is achieved. The use of prealloyed powders slightly improves the physical properties of sintered compacts, including density. Volumetric changes during sintering can be reduced effectively in the compositions low in tin, whereas in the tin-rich materials shrinkage of prealloyed compacts practically equals that of mixed powder compacts.

Method.—When comparing the cold-press and hot-press methods, the superiority in density and hardness of hot-molded materials is most striking. Using the relatively low temperature of 500°C., completely dense alloys with a hardness comparing favorably with wrought metal are obtainable. On the other hand, the die life at such temperature is still reasonably long for high hot-strength alloy steels. At the same time high strength and ductility are achieved if proper care is taken to make alloying effective. Possibly all these properties can still be improved if higher molding temperatures are employed.

The hot-press method offers definite possibilities for the production of certain solid bronze parts and bearings, where closest tolerances, high density and good mechanical properties or corrosion resistance are required, and Jones[16] has shown that industrial quantities of these parts can be made by employing the right type of equipment. In the manufacture of porous parts, such as self-lubricating bronze bearings, the conventional cold-press and sintering process has its established merits. However, the experimental results show that a porous bronze of the 90-10 composition with about 25 per cent porosity and a hardness of about 50 Brinell needs approximately 20 tons per sq. in. briquetting pressure against 2 tons per sq. in. or less when hot-pressed at or above 500°C. At the same time the entire sintering and final sizing operation can be eliminated. Hence the possibility of utilizing presses of very low capacity suggests close study of the applicability of the hot-press method for the production of certain porous parts of special design.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the American Electro Metal Corporation for the permission to publish the results of this investigation. He is indebted to Mr. H. A. Dorfman, chemical engineer of that company, for aid in making the diagrams and photomicrographs.

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DISCUSSION

(F. N. Rhines presiding)

E. V. CRANE.*—I want to ask Dr. Goetzel concerning the control of atmosphere in heating and pressing. Was the heating and pressing done in the die, or were the two kept separate there?

C. G. GOETZEL.—The setup used for this investigation implied heating the die to the temperature at which the work was to proceed, introducing a preformed compact into the hot die. The atmosphere was supplied through an annular chamber from which it passed through two holes into the die cavity.

E. V. CRANE.—The compact was not preheated?

C. G. GOETZEL.—The compact was not preheated.

THE CHAIRMAN.—In the course of recent studies on the effect of time of heating upon the tensile strength and hardness, I have observed that there is often a maximum in tensile strength and hardness reached before complete homogenization has been attained. The magnitude of each mechanical property changes rapidly with time in the early stages of sintering, the more so as temperature increases. For these reasons it seems that the comparison of values obtained by heating for the same time at a series of temperatures may be deceptive. Not only may those heated at higher temperatures give higher tensile readings, but the reverse may be true if the maximum in the tensile strength versus time curve has been passed. A better basis for comparison would be that of equal degree of diffusion.

C. G. GOETZEL.—Thank you, Professor Rhines, for this interesting contribution. I would like to add here that I have noticed a similar effect with straight copper.

There is, of course, the possibility that this maximum in hardness and tensile strength may be caused by work-hardening.

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* E. W. Bliss Co., Brooklyn, N. Y.

J. J. Cordiano.*—Some tests were conducted a few years ago on the hot pressing of green copper-powder compacts in a hydrogen atmosphere. In these tests the pressure was maintained constant at 20 tons per square inch and the temperature maintained constant at 600°C. The time at pressure and temperature was maintained for intervals of 4, 8, 16, 32 and 64 seconds.

The results of these tests indicated that with increasing time at temperature the hardness of the sintered compacts decreased. The tensile strength increased for the 4, 8, and 16-sec. tests but decreased from there on. The elongation increased from approximately 2 per cent for 4 sec. to 35 per cent for 64 seconds.

These test results and examination of the microstructure of the test specimens point to recrystallization of the grain structure and annealing of the compacts with increasing time as the cause for the drop in hardness and tensile strength.

C. G. Goetzel.—The time factor in hot pressing is very interesting, but an intelligent evaluation of its influence must await publication of Mr. Cordiano's paper. Although it appears that the time factor is very important in consolidating the compacts, the experiments of this study were confined to a relatively short time (60 sec.) during which the compact was kept under pressure. This was done because of some commercial possibilities. Production rates implying more than one to two minutes at heat and at pressure are probably possible only for very large pieces. On the other hand, one of the main handicaps in the development of the hot-press method has been so far that even for a short time at which pressure and heat are applied, say of the order of one minute or even half a minute, production rates are still too small to compete favorably with the present cold-press and sintering methods. However, if one would know the exact relationships between time and these properties perhaps in certain cases there would be a possibility of applying a somewhat longer time for this treatment.

G. F. Taylor.†—Over the past years I have seen a few references (for example, in the *Scientific American* Encyclopedia of Notes and Queries), to some such processes as that of forming rigid metallic bodies from amalgams and afterward driving off the mercury with heat. It is my impression that this general idea has never been fully exploited nor even systematically investigated with the view of finding out how many applications and ramifications it may have. For example, I have been doing some experimenting on a process which we call "cold welding."

A weld of this kind can be done at ordinary temperatures. Such a weld is as strong as a weld made by the ordinary process. In fact, there are patents covering such a process, Weder Patents 2094482 and 2094483. The weld, whether it refers to the cohesion between relatively large metallic surfaces or between the infinestimal particles of a powder, is the same phenomenon, just as the sintering of the powder of a metal without a cementing bond of lower melting point is also a form of welding.

The powder can be amalgamated either with mercurous nitrate or metallic mercury. Mercurous nitrate works better with any metal that is attacked by nitric acid but for others, such as the noble metals, metallic mercury must be used, but it should be used sparingly. After the powder has been amalgamated, it is compacted to its density in a powerful hydraulic press. A pressure of 100 tons per square inch is not too much. The greater the pressure, the smaller the amount of mercury needed to accomplish welding. After this, the compact is treated in an atmosphere of pure hydrogen at about 180°C. Although more than 200°C. below its boiling point, the vapor pressure of mercury at this temperature is 0.80 cm., so that it will evaporate from a small compact in a few hours. If the temperature is raised above the boiling point, the object is likely to crack, although the last traces can be expelled with strong heat.

Objects of intricate design could probably be submerged under a fluid and pressed hydraulically.

This method, it seems to me, offers possibilities of fabricating objects that would be very difficult to produce otherwise, and is to be recommended in almost any case in which the metallic ingredients are susceptible to amalgamation. Since amalgams of almost any metal, even iron, can readily be produced, I have often wondered if such metals as iron could be better produced from their amalgams than from the dry metal powder in the art of powder metallurgy.

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* Hardy Metallurgical Co., New York, N. Y.

† Carboloy Company, Detroit, Michigan.

C. G. GOETZEL.—As far as I know, there has been some work done with amalgams, primarily to form some alloy powders or to use mercury as a catalyst to bring together certain metals that would not readily diffuse otherwise. The metals are amalgamated and the mercury then distilled off. To use mercury in compacting and in heat-treatment appears to be somewhat dangerous because free mercury reacts with many metals rather strongly. On the other hand I believe one would need a larger proportion to form a binder that would give an effective cementing action. In spite of the danger to dies and furnace retorts when working with mercury and its vapor, an investigation of amalgamated powders may show very interesting results.

The Sintering of Metal Powders—Copper

By C. J. Bier,* Junior Member A.I.M.E., and J. F. O'Keefe*

(New York Meeting, February 1944)

This study was carried out with copper because it represents the simplest form of sintering, in that but one metal is involved and all reactions occur in the solid state.

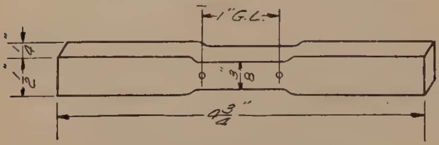

Fig. 1.—Tensile bar.

The present work will cover three variables affecting the sintering process; namely, briquetting pressure, sintering temperature and time in hot zone. Although strength and dimensional changes were observed, this is primarily a metallographic study of the sintering process in copper. The term "sintering" should be understood to mean the process by which the metal powder particles of the compact become united into one body.

Material Used

The copper powder used was made from reduced copper oxide, and is typical of a grade used for the mass production of parts formed of metal powders. The screen analysis of the powder was as follows:

Particle Size Mesh	Per Cent by Weight	Particle Size Microns	Per Cent by Weight
/80....	0.00	43/32....	17.49
80/100....	0.02	32/20....	16.68
100/140....	0.34	20/10....	23.14
140/200....	15.25	10/5.....	4.64
200/230....	5.00	5/0......	0.75
230/325....	16.70		
−325....	62.69		

The minus 325-mesh analysis was made by using a Roller Air Analyzer.[1,2]

The apparent density is here defined as the weight per cubic centimeter of the loose, unpacked powder as measured with the Hall flowmeter. The value for the powder used was 2.57 grams per cubic centimeter.

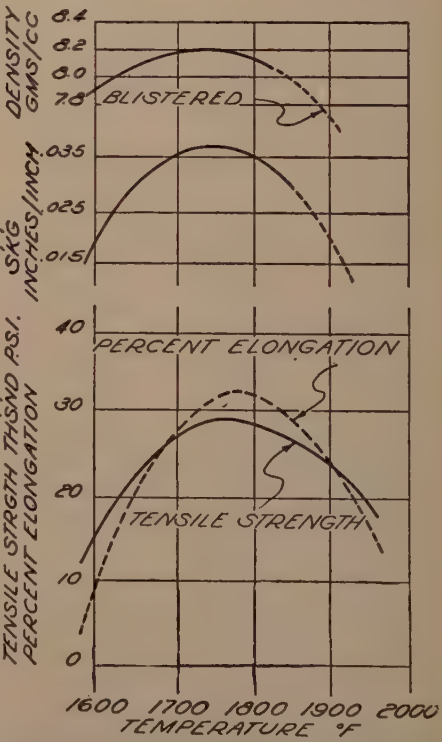

Fig. 2.—Effect of sintering temperature upon properties of copper-powder tensile bars briquetted from reduced oxide copper powder at 60,000 pounds per square inch and sintered for 30 minutes.

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* Metallurgists, H. L. Crowley and Co., Inc., West Orange, New Jersey.

[1] References are at the end of the paper.

The flow of the powder is here defined as the time in seconds required for 50 grams of the powder to flow under the influence of gravity through the Hall flowmeter. The value for the powder used was 27.5 seconds.

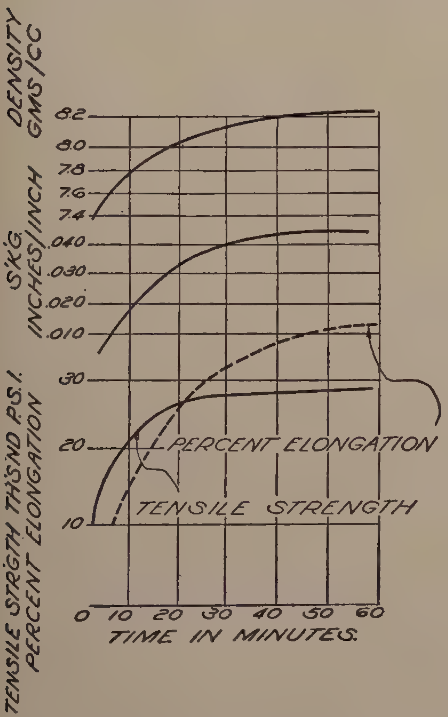

Fig. 3.—Effect of sintering time upon properties of copper-powder tensile bars briquetted from reduced oxide copper powder at 60,000 pounds per square inch and sintered at 1750°F.

Experimental Procedure

The general premise as regards the method of conducting the study was to maintain two of the three variables constant and change the third. The work on the effect of briquetting pressure was done at a constant temperature for a definite time; the effect of sintering temperature was observed at a definite briquetting pressure with a constant sintering time; the effect of sintering time was examined at a definite briquetting pressure and sintering temperature

To prevent seizing and galling of the die during briquetting, 1 per cent by weight of zinc stearate was mixed with the copper. This mixture was run through an 80-mesh screen to break down lumps in the lubricant and finally was mixed in a tumbler for 15 min. to distribute the lubricant evenly.

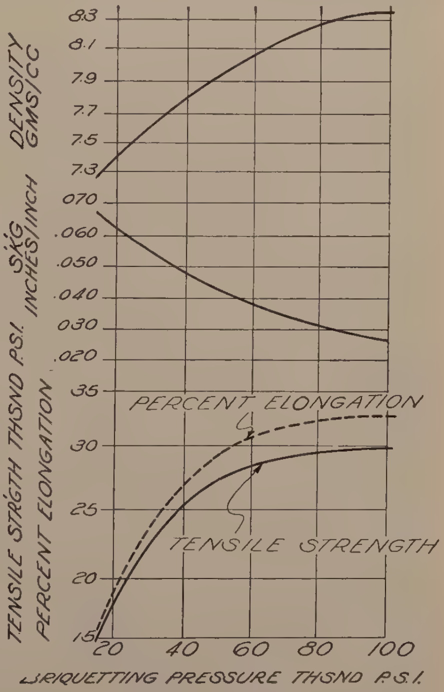

Fig. 4.—Effect of briquetting pressure upon properties of copper tensile bars from reduced oxide copper powder, sintered at 1750°F. for 30 minutes.

The die used to briquette samples for this study was in the form of a flat tensile bar, which yielded a briquette of the dimensions shown in Fig. 1.

Using a constant powder weight, it was found that the dimensional variations in length and width between successive green briquettes did not exceed 0.0002 in. and that the green thickness depended on the briquetting pressure. The rate of loading

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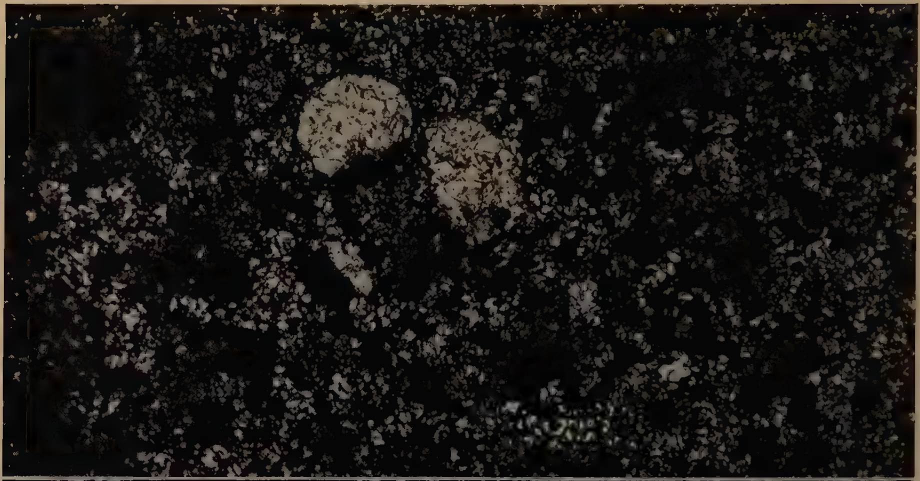

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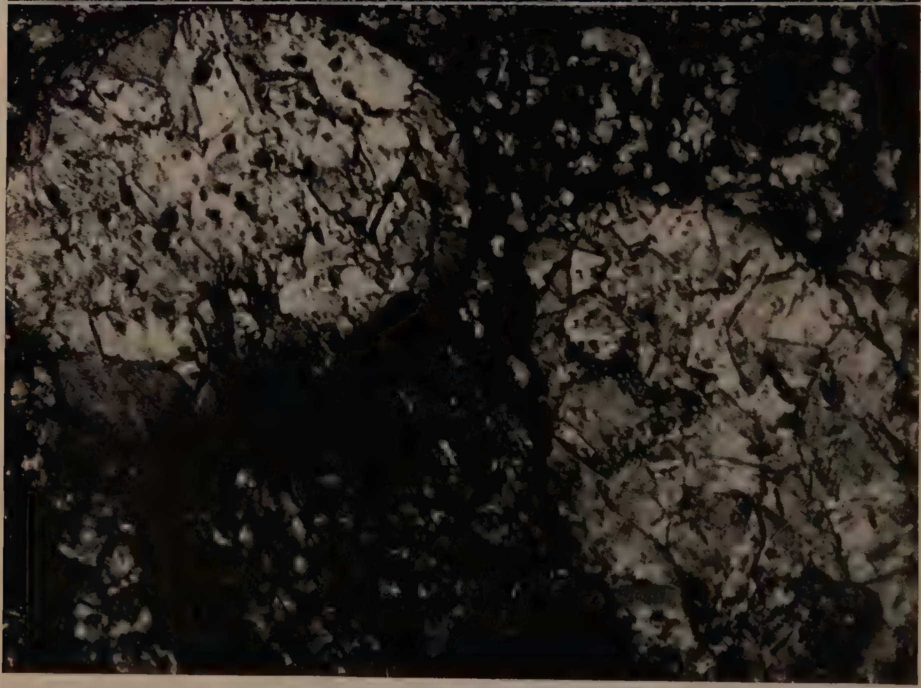
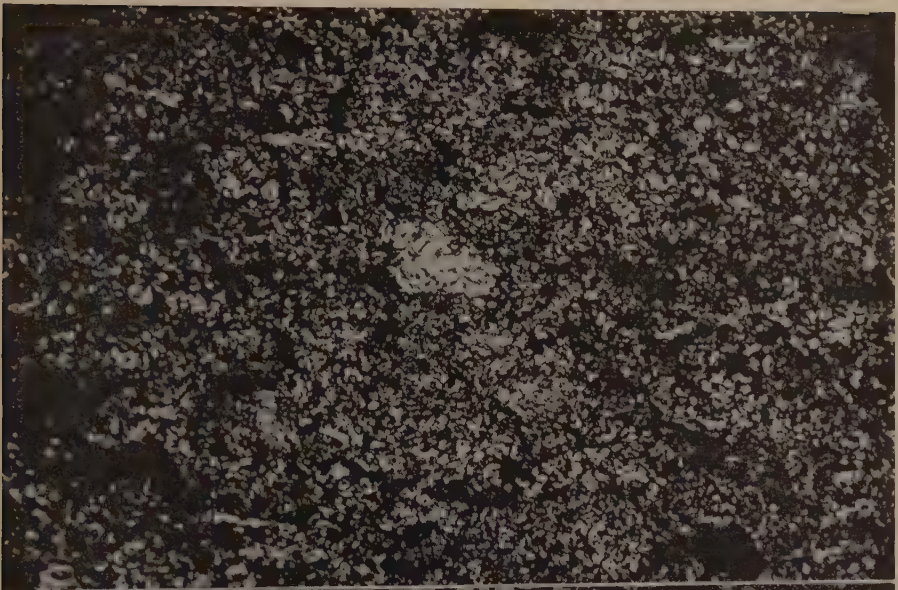


FIG. 5.—GREEN BRIQUETTE. × 200.
FIG. 6.—GREEN BRIQUETTE. × 750.



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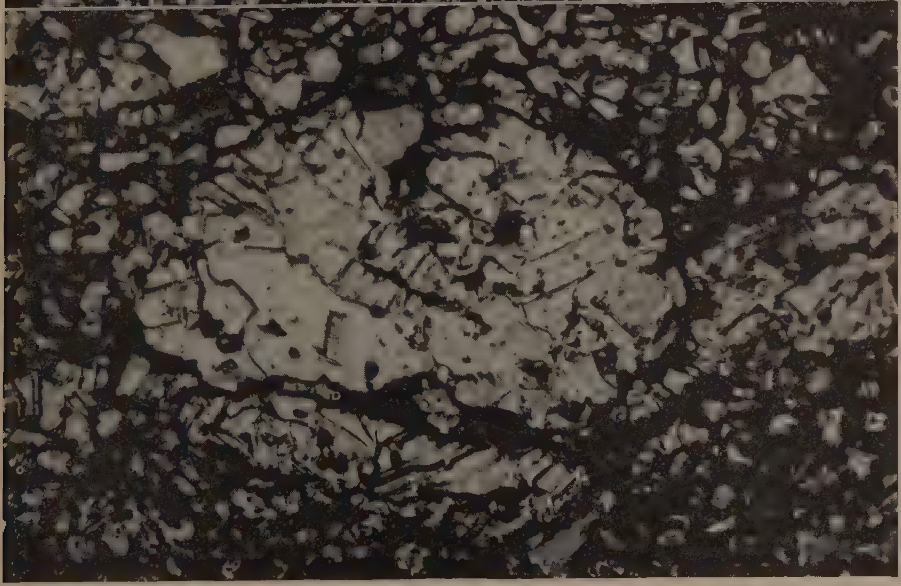

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FIG. 7.—1750°F., 2 MINUTES. × 200.
FIG. 8.—1750°F., 2 MINUTES. × 750.

while briquetting was held constant at 80,000 lb. per min. throughout the entire study.

Sintering was done in open boats placed in an electric furnace served with an atmosphere furnished by a commercial gas generator that cracked city gas at an air-gas ratio commonly used in the industry. While the furnace was equipped with a cooling zone, it did not have a preheat zone, consequently the briquettes were placed directly into the hot zone of the furnace, which had previously been brought to the desired sintering temperature. This point will be discussed later in regard to its effect on the sintering process. After sintering, the briquettes, were always pushed back at the same rate to a certain point in the cooling zone and left there until at room temperature. The same atmosphere was used in the cooling chamber as in the hot zone.

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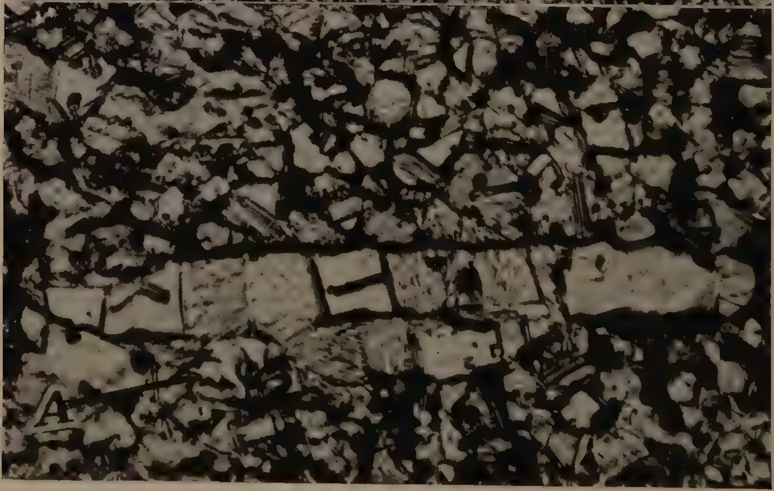

Fig. 9.—1750°F., 8 minutes. × 200.
Fig. 10.—1750°F., 8 minutes. × 750.
A, merging of particles.

The study on the effect of temperature on the sintering process was conducted with the furnace at the following temperatures: 1550°, 1600°, 1650°, 1675°, 1700°, 1725°, 1750°, 1775°, 1800°, 1850°, 1900°, and 1930°F. Sintering time was held constant in this part of the study at ½ hr. with the work probably at temperature after 5 min. in the furnace. Briquetting pressure was uniformly 60,000 lb. per sq. inch.

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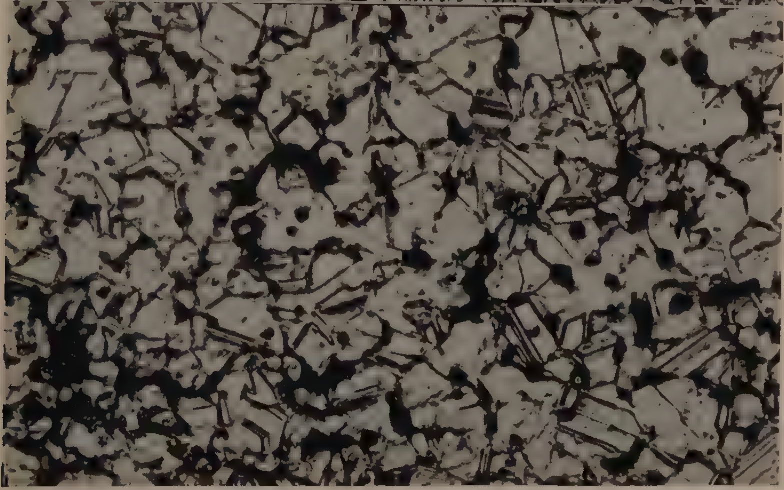
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FIG. 11.—1750°F., 12 MINUTES. × 200.
FIG. 12.—1750°F., 12 MINUTES. × 750.

The study on the effect of time was conducted with the following time intervals: 2, 4, 6, 8, 10, 12, 20, 30, 40, 50 and 60 min. These represent total time in the hot zone of the furnace and are not to be taken as time at temperature. The temperature of the furnace throughout the time study was 1750°F. The briquetting pressure used was 60,000 lb. per sq. inch.

The study on the effect of briquetting pressure was conducted at pressures of 20,000; 40,000; 60,000; 80,000 and 100,000 lb. per sq. inch. The furnace temperature was 1750°F. and the total time in the hot zone of the furnace was ½ hr. for all samples.

Tensile strengths and elongations were obtained without sizing or machining and are reported as sintered. Representative samples were obtained from each bar for metallographic examination. Tensile strengths, elongations, shrinkages and densities are reported in Figs. 2 to 4. The etchant used throughout the study was 10 per cent ammonium persulphate.

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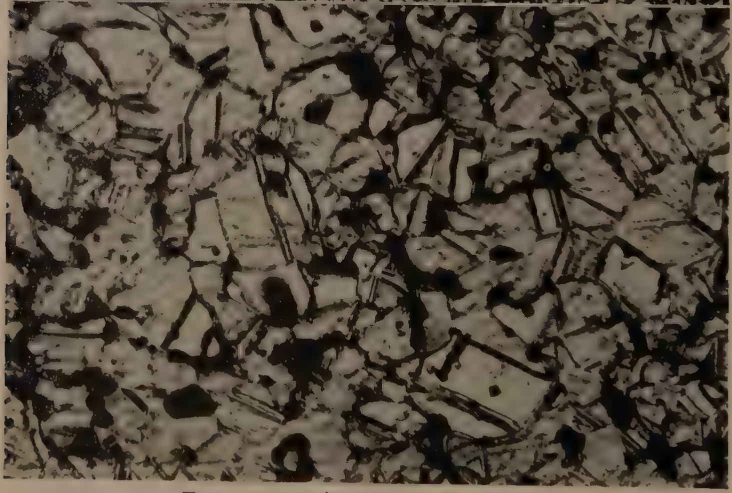
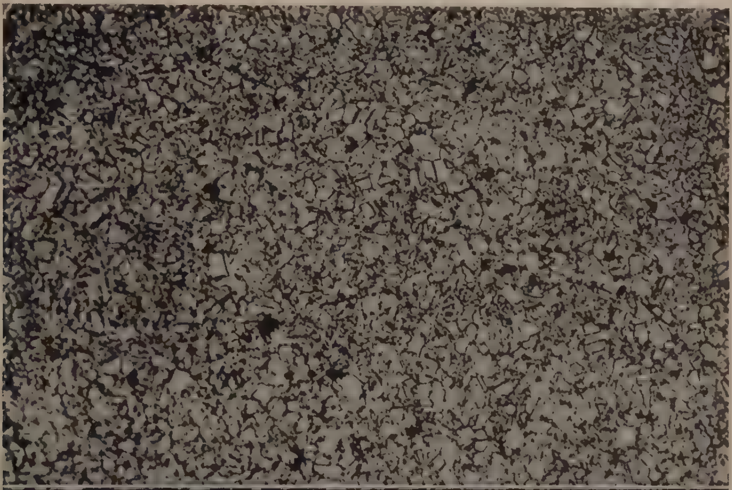


Fig. 13.—1750°F., 20 minutes. × 200.
Fig. 14.—1750°F., 20 minutes. × 750.

Discussion of Results

When copper powders are briquetted, the particles are brought into close contact, many of the oxide coatings are broken and considerable deformation occurs,[3] resulting in more areas of contact, all of which tends to make a fairly strong part. The oxide coatings are commonly found in hydrogen-reduced copper powders. It has been found that most copper briquettes have a thin shell of cold-worked and distorted particles while inside that shell little if any distortion of the particles can be seen. It is important to note that if the cold-worked shell is removed from the green briquette by machining, a great deal of the strength is lost. The shell is caused by high surface friction between the die and the powder. Figs. 5 and 6 are photomicrographs of the interior of a green briquette. Attention is directed to the difference in size of the particles; several large particles can be observed surrounded by smaller ones. Also, the particles retain their identity, though pressed, each being outlined by its particle boundary. Copper-powder particles are not necessarily single-grained; indeed, a single-grained particle usually is found only in the minus 325-mesh powder.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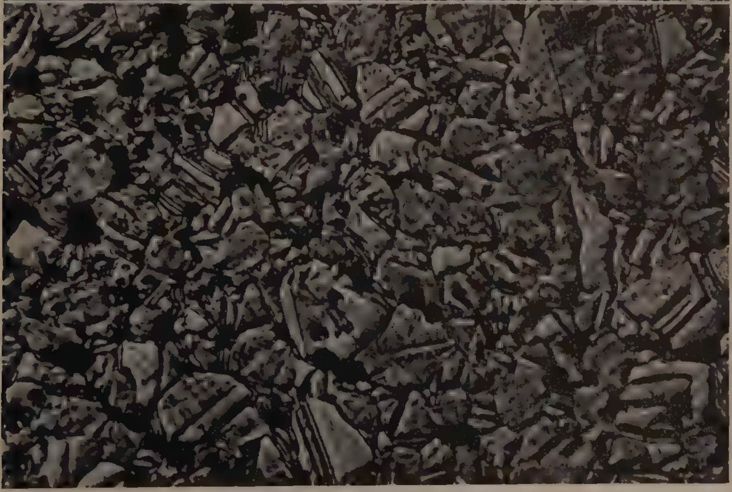
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Fig. 15.—1750°F., 30 minutes. × 200.
Fig. 16.—1750°F., 30 minutes. × 750.

The welding or union of the particles in briquetting is probably similar to that observed at interfaces when processing alclad sheet, bonding of silver,[16] cold-welding of gold,[17,18] or similar processes.

Work in the authors' laboratory on very low sintering temperature, or at very short times at usual sintering temperatures, shows that while no changes can be observed in the microstructure there is a noticeable increase in tensile strength, elongation, density and dimensional change.

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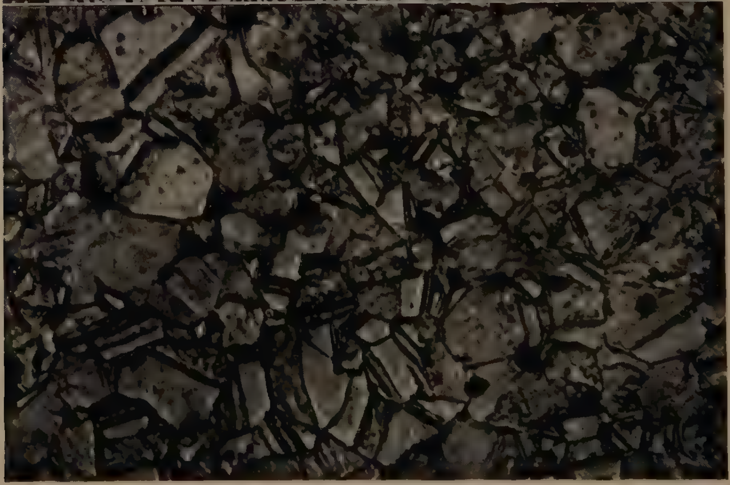
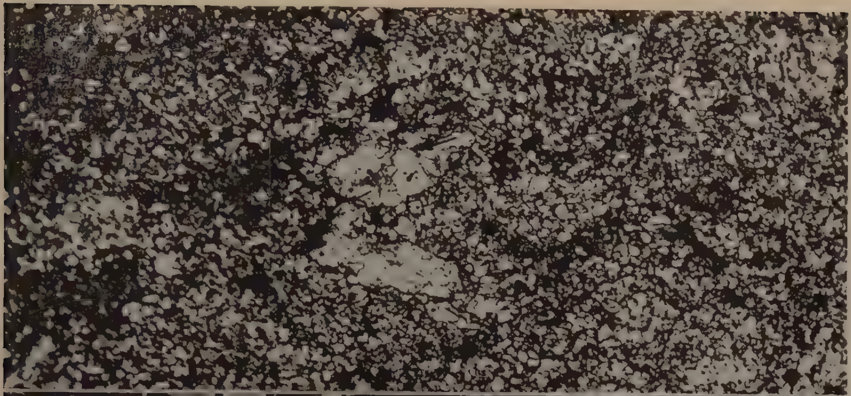


Fig. 17.—1750°F., 60 minutes. × 200.
Fig. 18.—1750°F., 60 minutes. × 750.

As the sintering temperature is raised, or somewhat longer sintering times at higher temperatures are used, there is a marked increase in strengths and other properties, as reported in Figs. 2, 3 and 4. These changes are reflected in the microstructure. Figs. 7 and 8, of a copper briquette after 2 min. at 1750°F., and Figs. 19 and 20, of a copper briquette after 30 min. at 1550°F., all give evidence of a spread of the bonding areas between particles as a result of the reduction of the oxide coatings by the atmosphere used in sintering.[14,15] All of these photomicrographs contain large and small particles.



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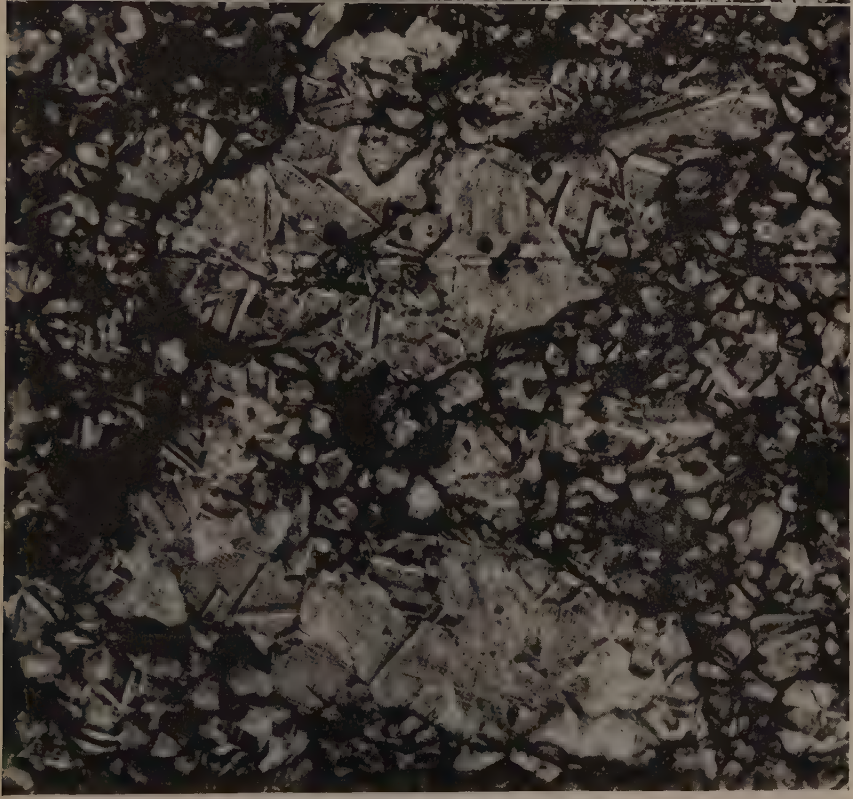

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Fig. 19.—1550°F., 30 minutes. × 200.
Fig. 20.—1550°F., 30 minutes. × 750.

At still higher temperatures or longer times, a merging of adjacent particles can be observed microscopically; as, for example, in Figs. 9 and 10, of a copper briquette after 8 min. at 1750°F., and Figs. 21 and 22, of a copper briquette after 30 min. at 1650°F. Particular attention should be paid to the large particles in the center of each of these photomicrographs, in contrast with the smaller particles around them and the manner in which these particles have merged at their boundaries with the smaller particles. The merging of adjacent particles results in further increases in tensile strengths, elongation, density and dimensional change, as reported in Figs. 2, 3, and 4. In connection with these microscopic and physical changes, the work of Wretblad and Wulff[4] gives an important description of their occurrence.

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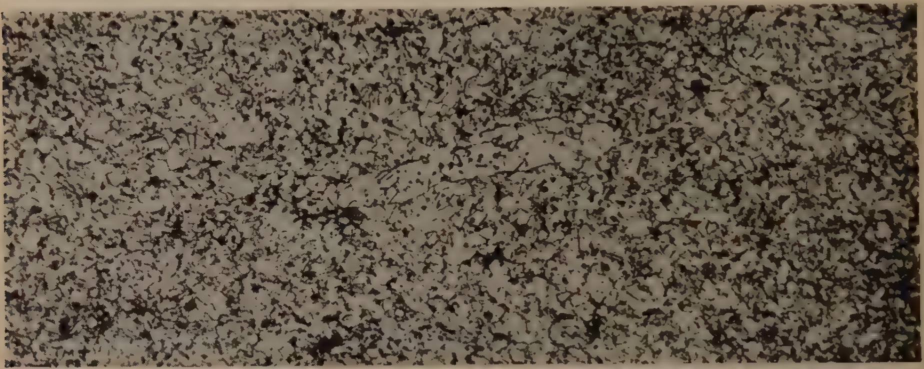

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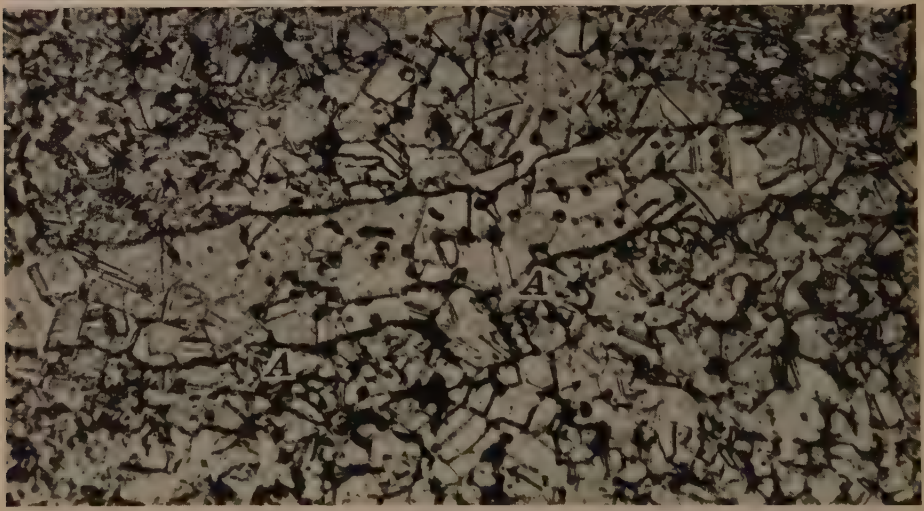
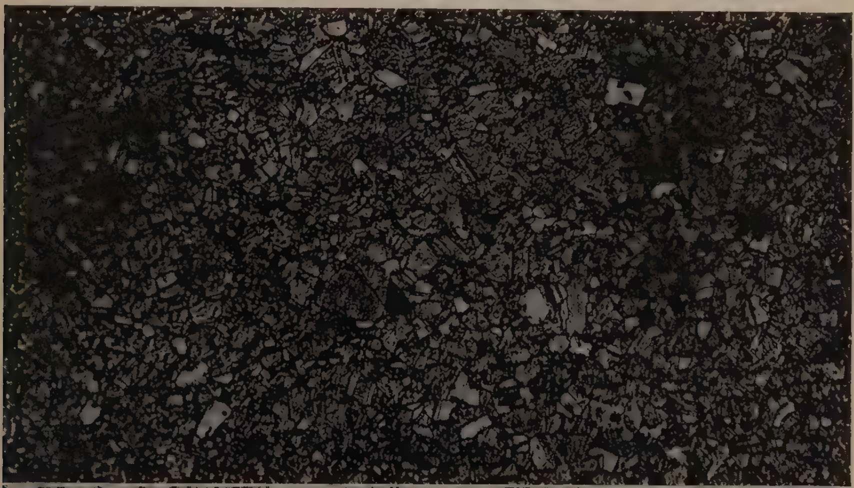


Fig. 21.—1650°F., 30 minutes. × 200.
Fig. 22.—1650°F., 30 minutes. × 750.
Original magnification given; reduced one third in reproduction.
A, merging of particles.

In following the progress of the sintering process microscopically, a very narrow range of temperatures and times is reached within which an entirely new aspect of the microstructure appears. Up to this range, while reduction of the oxide coatings and merging of adjacent particles had been observed, the structure consisted of a nonuniform mass of large and small particles (Figs. 7 to 10). Within the narrow range of temperatures and times mentioned, the structure becomes more uniform in regard to grain size, the identity of the large and small particles is lost, and a general increase in grain size is observed; the structure resembles that of a cast, wrought and annealed copper. Figs. 11 and 12 illustrate this new structure. Such structures were observed in the time studies after 12 min. at 1750°F., while in the temperature studies they appeared at about 1650°F. for 30 min. There can be no doubt that this change in structure from a nonuniform area of large and small particles to a uniform one where the original particles have lost their identity is caused by a general recrystallization of the briquette.[5–10]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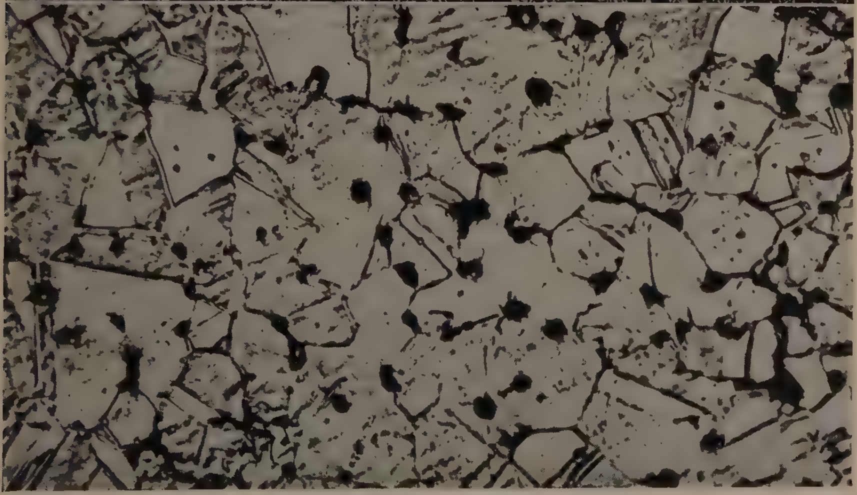
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FIG. 23.—1850°F., 30 MINUTES. × 200.
FIG. 24.—1850°F., 30 MINUTES. × 750.

Up to this point no mention has been made of porosity, because this seemed the

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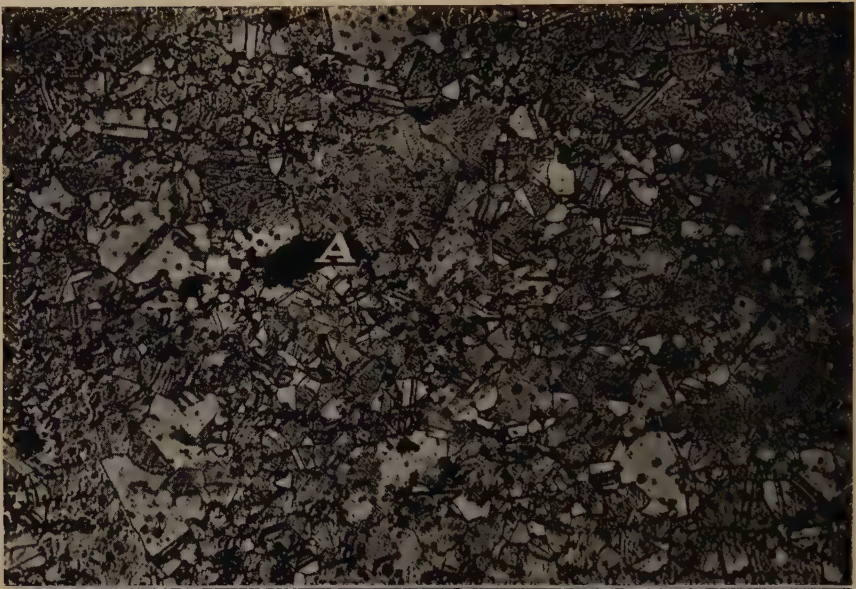

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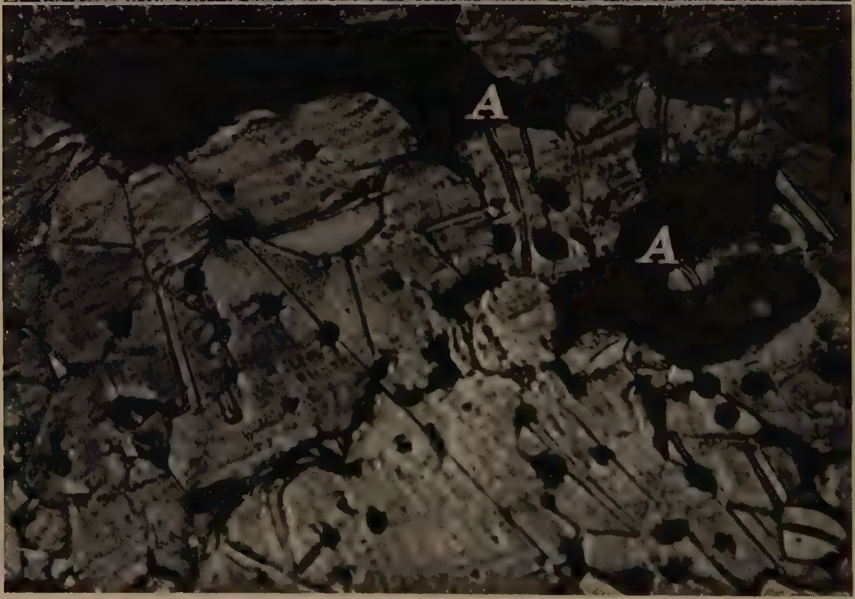

FIG. 25.—1930°F. × 200.
FIG. 26.—1930°F., 30 MINUTES. × 750.
A, blisters.

most suitable place to discuss it. A copper-powder particle contains pores, the degree of porosity varying with the manufacture. When the powder is briquetted a different type of pore is formed, the interparticle pore—the space between particles, which is formed by the areas not in contact. These two types of pores, the intraparticle pore and the interparticle pore, persist as distinct entities up to the recrystallization range. It would be very difficult to study the effect of the progress of the sintering process on the intraparticle pore but the effect on the interparticle pore can be observed microscopically. The shape of the interparticle pore changes from a y-type to an oval type during sintering,[4] such changes being noticeable in Figs. 7–12, inclusive. There is a steady decrease in interparticle pore size up to the recrystallization range. In that range, with the change from a nonuniform structure to a uniform one, the distinction can no longer be made between intraparticle and interparticle pores. It is important to note that the interparticle pore can be used as a means for distinguishing the outlines of a given particle.

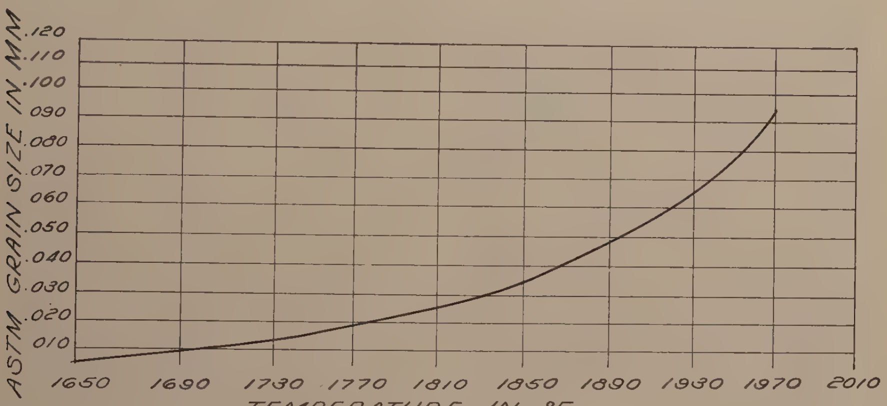

FIG. 27.—EFFECT OF FURNACE TEMPERATURE ON GRAIN SIZE OF COPPER-POWDER BRIQUETTES SINTERED ONE-HALF HOUR IN HOT ZONE.

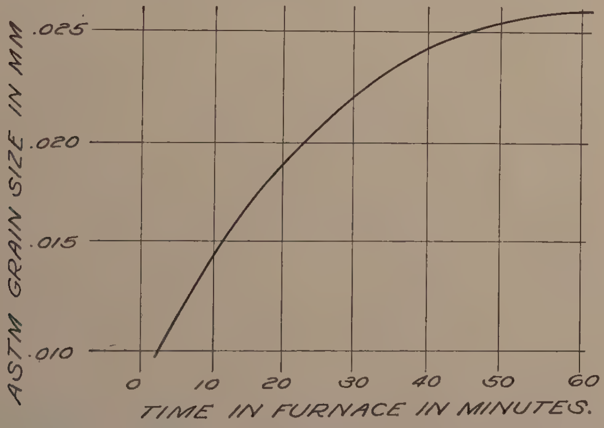

FIG. 28.—EFFECT OF TIME IN FURNACE ON GRAIN SIZE OF COPPER-POWDER BRIQUETTE SINTERED AT 1750°F.

Increasing the sintering temperatures beyond those so far discussed results in large increase in grain size[7-10] as seen in Figs. 23 and 24, 30 min. at 1850°F., and Figs. 25 and 26, 30 min. at 1930°F. However, it can be observed in Figs. 15 and 16, 30 min. at 1750°F., and Figs. 17 and 18, 60 min. at 1750°F., that further increase of time in the furnace causes very little if any increase in grain size; compare with Figs. 13 and 14, 20 min. at 1750°F. Figs. 27 and 28 also illustrate this point. This grain-size increase leads to a general drop in tensile strength, elongation, density and dimensional changes—Figs. 2, 3 and 4.

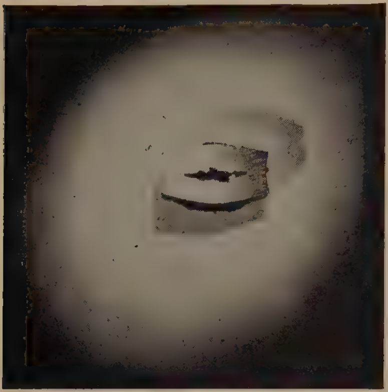

FIG. 29.—BLISTER. FULL SIZE. PHOTOMACROGRAPH.

However, the increase in grain size is not the only reason for the change in physical properties. The rate of heating of the sample has a very important effect on the sintering process; when the samples were placed in a furnace at the higher temperatures used in this study, the rate of heating was very high. When a briquette is subjected to such a high heating rate, the die lubricant, products of decomposition of the oxide coatings, and entrapped gases are in effect sealed in the sample before they have a chance to escape. If the rate of heating is fast enough, these factors build up a considerable internal pressure in the sample, and finally may blister or cause the appearance of surface bumps, which increase in size until they burst. Fig. 26 is of an incipient blister, while Fig. 29 is part of an external blister. Under these conditions the porosity becomes very high, aside from blistering, which possibly may be due to liquation.

The effect of briquetting pressure is most obvious in regard to porosity—increasing briquetting pressures decreases the porosity. The tensile strength, elongation and density are increased by increasing briquetting pressure, while the shrinkage decreases (Fig. 4). The decrease in porosity probably accounts for the greatest part of the increase in tensile strength. Microscopic examination does not show significant grain-size differences among the sintered structures briquetted at the various pressures covered in this study.[12,13]

SUMMARY

A metallographic study of the mechanism of the sintering process in copper powder has been made, illustrating the structural changes that occur as a pressed powder bar is sintered.

ACKNOWLEDGMENT

The authors wish to thank Mr. H. L. Crowley, of H. L. Crowley and Company, Inc., for his kind permission to publish this work. They greatly appreciated the sympathetic encouragement of Mr. E. S. Patch and are much indebted to Dr. F. N. Rhines for his straigh forward and careful analysis of this paper as well as for his stimulating discussions of it.

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Some Experiments on the Effect of Pressure on Metal-powder Compacts

By Jerome F. Kuzmick*

Many investigations have been made on the effect of the variables of pressure, sintering temperature and sintering time on the physical and microstructural characteristics of metal-powder compacts. Several such investigations have indicated that pressure is the least important of these three factors in an attempt to secure a dense, strong compact by a simple cold-pressing and sintering procedure. However, it was felt that a further study of the effect of pressure on pressed and sintered metal-powder compacts might prove interesting, for the following reasons:

1. In work done in the past on the effect of pressure, temperature, and time, the metal-powder compacts were subjected to long sintering periods, and temperatures right up to the melting point of the metal were applied. It was thought that pressure might exert a more profound effect under short-time sintering and within narrower ranges of temperature, such as normally would be applied in large-scale production of metal-powder parts.
2. It was hoped that something further might be learned of the nature of the bond in pressed and sintered metal-powder compacts.
3. It was thought that interesting information concerning the work-hardening effect of pressure on the crystal structure of sintered metal-powder compacts would be obtained.

PROCEDURE

Rectangular bars, 2 by ½ by ¼ in., were molded from the following metal powders:

Atomized tin powder, 325-mesh
Atomized aluminum powder, 325-mesh
Reduced copper powder, 100-mesh
Electrolytic iron powder, 100-mesh
Atomized 70-30 brass powder, 100-mesh

The tin powder was molded at various pressures up to 40 tons per sq. in. This was the maximum, because at higher molding pressures there was considerable extrusion of tin into the die wall, jamming the die plungers. The tin specimens were not sintered, as this phase of the work was done merely to see how much a very soft metal could be compressed.

The aluminum powder was compressed at various pressures up to 50 tons per sq. in. Higher pressures could not be used because of extrusion into the die wall. The compacts were sintered one hour at 600°C. in pure dry hydrogen.

The copper powder was molded at various pressures up to 96 tons per sq. in. One set was sintered at 750°C., another at 950°C. for one hour in pure dry hydrogen.

The electrolytic iron powder was molded at various pressures up to 96 tons per sq. in. and sintered, one set at 800°C. and one set at 1300°C. for one hour in pure dry hydrogen. Extra 325-mesh specimens were also prepared to study the effect of reduced particle size on grain structure.

The brass powder was molded at various pressures up to 96 tons per sq. in. and sintered for one hour, one set at 650°C. and one set at 890°C., in pure dry hydrogen.

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* Assistant Director of Research, Stevens Institute, Hoboken, New Jersey.

The specimens were placed in a closed container during sintering to minimize zinc loss.

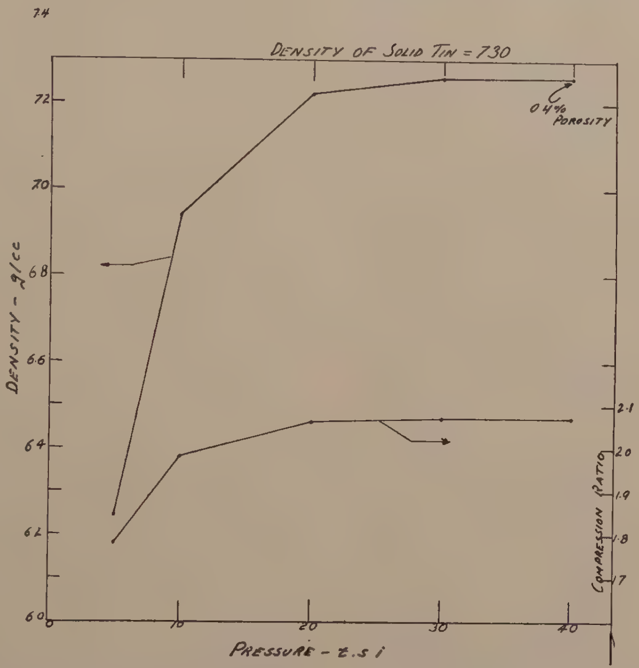

FIG. 1.—DENSITY AND COMPRESSIBILITY RATIO VS. PRESSURE OF TIN POWDER.

Density and hardness were determined on the unsintered specimens and the microstructure was studied.

Density, hardness, tensile strength, and elongation were determined on the sintered specimens and the microstructure was studied.

Originally, it had been planned to use dumbbell shaped tensile-test specimens but these would have allowed a maximum pressure of some 65 tons per sq. in. with the press available. The rectangular specimens allowed a maximum pressure of 96 tons per sq. in. The specimens were prepared for tensile and elongation determinations by machining a notch on each side to ensure their breaking at the center. The values are probably erroneous because of stress concentrations at the notches; however, since all specimens were broken under identical conditions, it was felt that a relative comparison could be made to ascertain the effect of pressure on these properties, which was the object of the experiment.

The results of this series of experiments are shown in the curves and photomicrographs.

TIN

Fig. 1 shows that the density of the compacts rises rapidly to a value of 7.2 at 15 tons per sq. in. It then rises slowly to 7.26 at 30 tons per sq. in. and remains at this value at 40 tons per sq. in. The conclusion was drawn, upon examining the extrusions, that the maximum densification occurred at 30 tons per sq. in. The maximum density of 7.26 corresponds to a porosity of 0.4 per cent based on a density of 7.29 for solid tin.

It thus appears that upon pressing a soft metal powder, such as tin, at increasing pressures, the density very closely approaches that of the solid metal, but does

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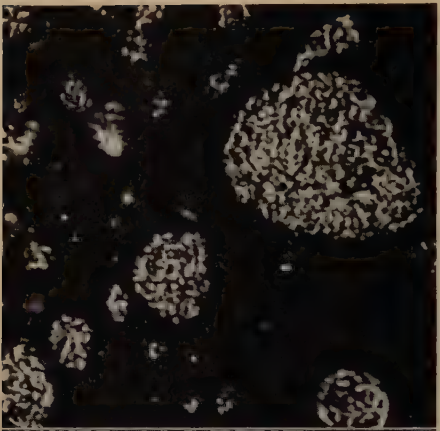

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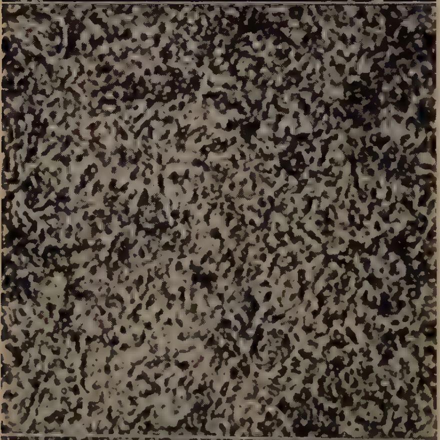

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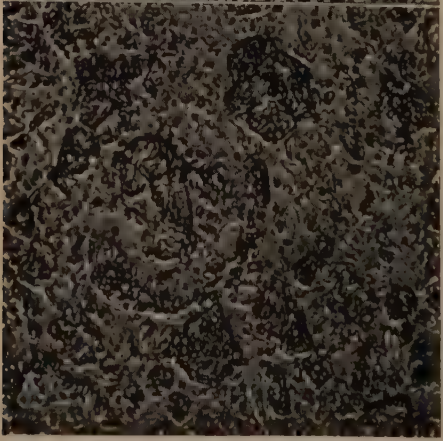

FIG. 2.—TIN POWDER. UNETCHED. × 1000.

FIG. 3.—TIN POWDER PRESSED AT 10 TONS PER SQUARE INCH. ETCHANT 10 PER CENT HCl. × 1000.

FIG. 4.—TIN POWDER PRESSED AT 30 TONS PER SQUARE INCH. ETCHANT 10 PER CENT HCl. × 1000.

not quite reach it. It might be that if the pressing could be done in a perfectly tight die, which would not allow extrusion to take place, solid density might be achieved. It might also be that actual solid blocks were obtained at 30 and 40 tons per sq. in., but that the density was a little below that of solid tin because of oxide inclusions resulting from oxide films on the powder. It would have been interesting to go to still higher pressures, but this could not be done because of the difficulty in removing the fins clearly from the specimen and cleaning the tin coating rubbed onto the die walls by the extruded material.

The curve for compression ratio, of course, follows the slope of the density curve, the numerical value going from 1.78 to 1 at 5 tons per sq. in., to 2.07 to 1 at 30 and 40 tons per sq. inch.

The photomicrographs (Figs. 2 to 4) show that a very interesting phenomenon has occurred. The specimen pressed at 10 tons per sq. in. merely shows the usual consolidation of metal powder under pressure, the particles being crowded together into close contact but retaining their original crystalline structure. However, the photomicrograph of the specimen pressed at 30 tons per sq. in., shows that *many of the original particle boundaries have disappeared*. Some of the original particles remain, embedded in a matrix of what apparently is recrystallized metal. High pressures applied to low-melting-point metallic particles evidently exert sufficient plastic deformation to cause recrystallization at room temperature. Of course, the recrystallization of the tin at room temperature by severe cold-working is nothing unusual. What is interesting is that the new crystals evidently have bridged and obliterated the original particle boundaries. It would be interesting to see whether extremely high pressure applied to higher melting metals would cause similar phenomena. This would then indicate the possibility of fabricating metal-powder parts by the use of pressure alone.

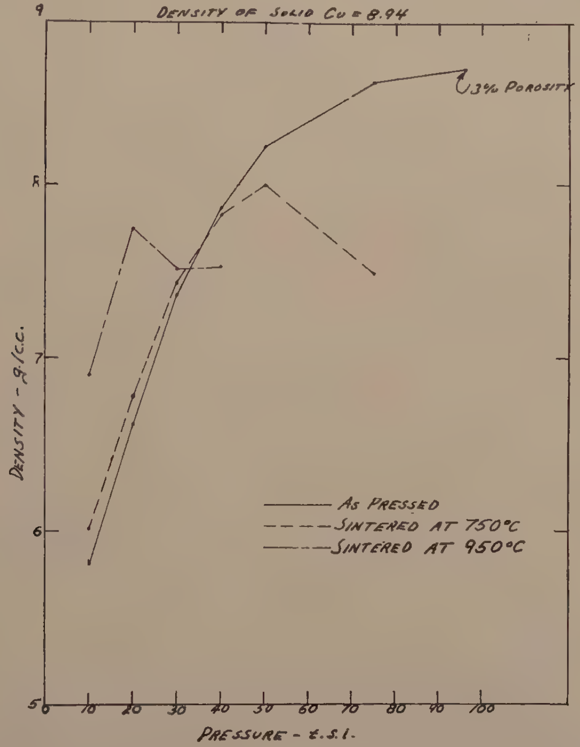

FIG. 5.—DENSITY VS. PRESSURE OF REDUCED COPPER POWDER.

From this study of the effect of pressure on tin powder, the following general conclusions can be drawn:

1. It is possible to cold-compress a metal powder to very close to theoretical solidity.

2. The use of high enough pressure will cause recrystallization to occur at room temperature when a low-melting metal powder is cold-pressed.

3. The recrystallization of a low-melting metal powder by cold compression obliterates the interparticle boundaries, resulting in massive fine-grained metal.

COPPER

Effect of Pressure on Density.—Fig. 5 shows that the density of compressed, unsintered copper powder follows the usual curve, increasing rapidly with increase in pressure in the lower pressure range, then flattening out at the upper pressure range. The porosity of the unsintered copper was 3 per cent at the maximum pressure used (96 tons per sq. in.).

The densities after sintering vividly illustrate the fact that the pressures that can be applied to reduced copper powder are limited because of the expanding effect of gaseous constituents during sintering. The specimens sintered at 950°C. showed considerable shrinkage at 10 and 20 tons per sq. in., slight shrinkage at 30 and expansion at 40 tons per sq. in. Those pressed at pressures higher than 40 tons per sq. in. were so swollen and blistered that density measurements were impossible. The specimens sintered at 750°C. showed slight shrinkage up to 35 tons per sq. in. and expansion at

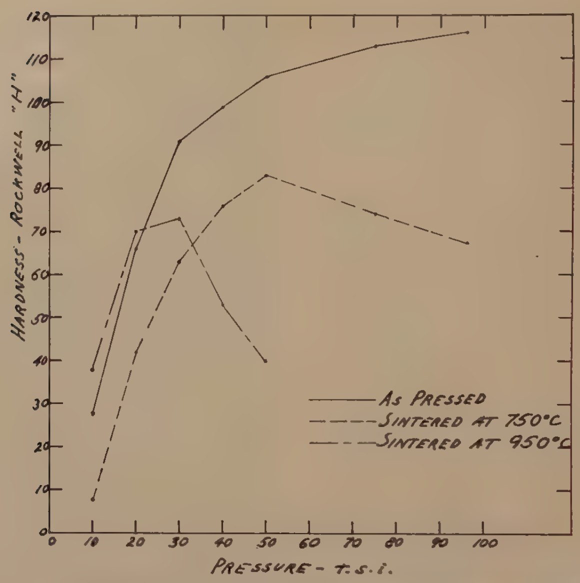

FIG. 6.—HARDNESS VS. PRESSURE OF REDUCED COPPER POWDER.

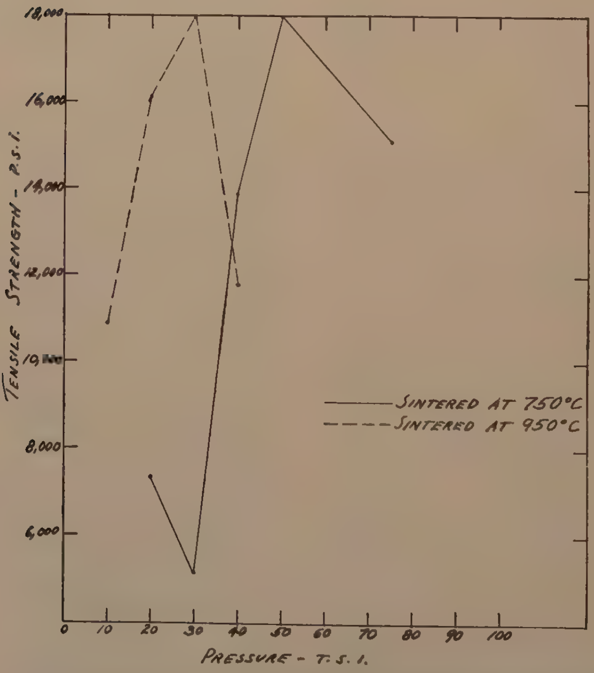

FIG. 7.—TENSILE STRENGTH VS. PRESSURE OF REDUCED COPPER POWDER.

pressures above that figure. The specimens pressed at 96 tons per sq. in. were too blistered to permit density determination.

Of the specimens sintered at 950°C., the specimen at 20 tons per sq. in. showed the highest density, 7.75. Of the specimens sintered at 750°C., the specimen at 50 tons per sq. in. showed the highest density, 8.00.

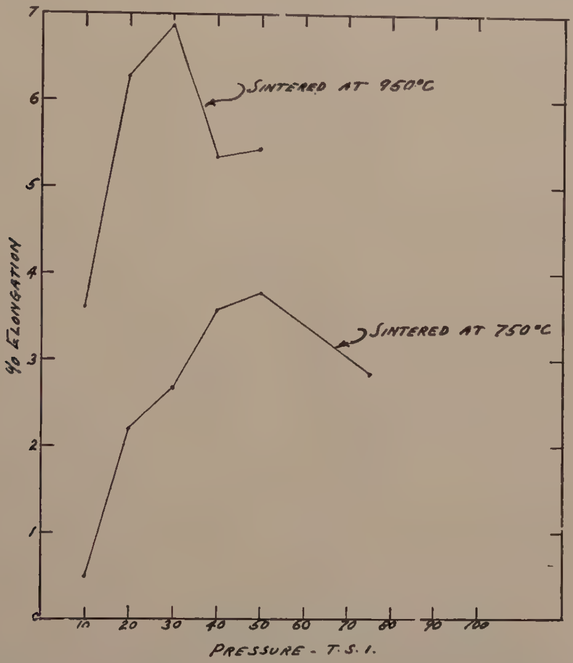

FIG. 8.—PER CENT ELONGATION VS. PRESSURE OF REDUCED COPPER POWDER.

Effect of Pressure on Hardness.—Fig. 6 shows that the hardness curves for both the unsintered and sintered specimens follow exactly the same trends as the density curves. The hardness of the "green" specimens increases with pressure to Rockwell H-116 at 96 tons per sq. in. Incidentally, the hardness readings were all made on the Rockwell H scale, even though this meant going over 100 on the unsintered specimens, so that a graphic comparison could be made between the hardnesses of the unsintered and sintered specimens. The hardness curves of the sintered specimens for both sintering temperatures follow the density curves almost exactly. The specimens sintered at 950°C. showed the highest hardness, H-73, at 20 to 30 tons per sq. in., with increase in hardness over the unsintered specimens up to 20 tons per sq. in. The specimens sintered at 750°C. showed the maximum hardness, H-83, at 50 tons per sq. in., with lower hardnesses throughout than on the unsintered specimens. The highest hardnesses were secured at the same pressures at the highest densities, indicating a close relationship between hardness and density.

Effect of Pressure on Tensile Strength.—Fig. 7 shows that the tensile strength is also closely related to the density. The highest tensile strengths were secured at exactly the same pressures, 30 tons per sq. in. for 950°C. sinter and 50 tons per sq. in. for 750°C., at which the maximum density values were secured. It is interesting to note that the highest tensile strength for the 750°C. specimens, 18,000 lb. per sq. in., is exactly equal to the highest tensile strength secured on the 950°C.

specimens. Since the 18,000 lb. per sq. in. specimen sintered at 950°C. was less dense than the 18,000 lb. per sq. in. specimen sintered at 750°C., this can be taken as an indication that the actual bond between particles is stronger with the higher sintering temperature.

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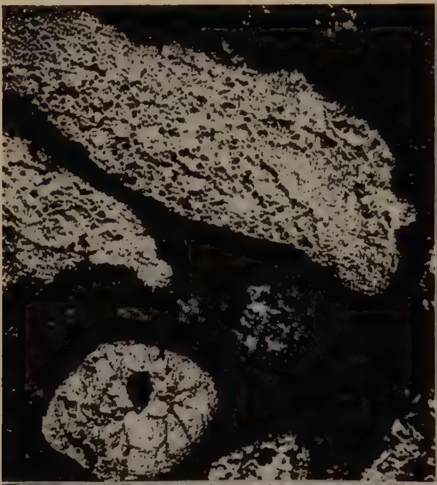

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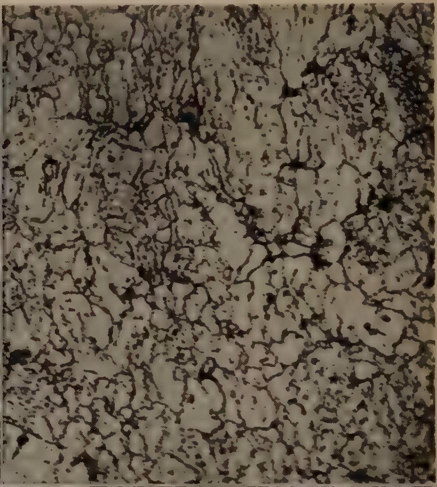

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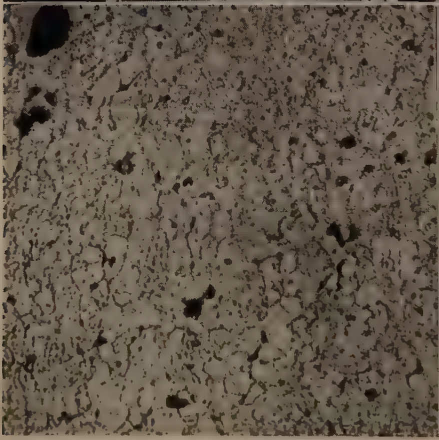

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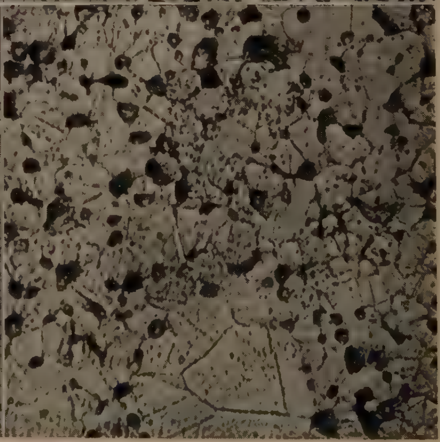

Fig. 9.—Copper powder. Unetched. × 500.

Fig. 10.—Copper powder pressed at 50 tons per square inch, unsintered. Etchant NH_4OH and H_2O_2. × 500.

Fig. 11.—Copper powder pressed 50 tons per square inch, sintered at 750°C. Etchant NH_4OH and H_2O_2. × 500.

Fig. 12.—Copper powder pressed 40 tons per square inch, sintered at 950°C.

Effect of Pressure on Elongation.—The elongation curves (Fig. 8) also show the maximum elongations at the same pressure, 30 tons per sq. in. for 950°C. sinter, 50 tons per sq. in. for 750°C., at which the maximum densities were secured, indicating a close relationship between ductility and density. It is important to note, however, that all the specimens sintered at 950°C. showed considerably more elongation than those sintered at 750°C.

Effect of Pressure on Microstructure.—Fig. 10, showing the microstructure of unsintered copper pressed at 50 tons per sq. in., reveals slight porosity, orientation of large particles normal to the direction of pressure, and flattening of the particles.

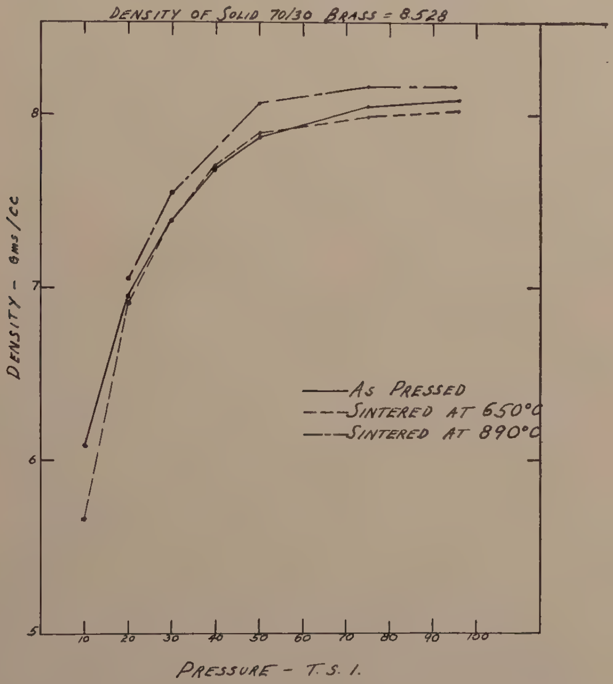

FIG. 13.—DENSITY VS. PRESSURE OF 70-30 BRASS POWDER.

Fig. 11, of the microstructure of the specimen pressed at 50 tons per sq. in. and sintered at 750°C., shows that most of the original particle boundaries remain. Some pore generation has occurred, but the structure does not differ very much from that of the unsintered specimen.

Fig. 12, the microstructure of the specimen pressed at 30 tons per sq. in. and sintered at 950°C., shows that considerable alteration of the grain structure has taken place upon sintering at this temperature. Most of the original particle boundaries have disappeared. Grain growth and twinning have occurred. Many pores have been generated. In certain sections, where pores are absent, the structure looks very much like that of ordinary annealed copper.

Conclusions.—From the work on copper powder, the following general conclusions can be drawn:

1. The pressure that can be applied to reduced copper powder in making compacts is limited if successful sintering without swelling and blistering is to be accomplished.

2. The physical properties of copper compacts—hardness, strength, and ductility—are closely related to the density.

3. For a given sintering temperature and time, a pressure can be determined that will give the maximum physical properties in a reduced copper-powder compact. Use of lower or higher pressures gives inferior properties.

4. A high sintering temperature is desirable if ductility is desired in copper compacts.

5. Higher sintering temperatures apparently strengthen the bond between

particles in reduced copper compacts, but the total effect is somewhat nullified by the generation of pores at these temperatures, which weaken the structure.

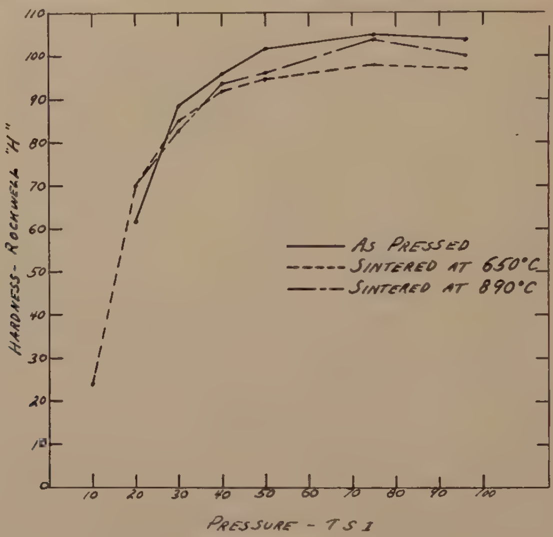

FIG. 14.—HARDNESS VS. PRESSURE OF 70-30 BRASS POWDER.

6. It appears that work should be done on controlling evolved gases in sintering reduced copper compacts, to prevent pore generation, if improved physical properties are to be obtained.

BRASS

The sintered specimens were weighed and measured and their densities computed. The Rockwell H hardness was determined on each sample. It was found that the specimens sintered at 650°C. were so weak that they all broke upon being machined. The 890°C. specimens were broken on the Tinius Olsen machine and unit tensile strengths were computed. The length of the specimens before and after breaking was measured, and the percentage of elongation was computed.

Effect of Pressure on Density.—Fig. 13 shows that the unsintered density increases with pressure, reaching a maximum at 96 tons per sq. in. of 8.09 (5 per cent porosity). Upon sintering at 650°C. there is practically no change in density. This would indicate that actual sintering has not started at this temperature, as there is no evidence of shrinkage. This statement, of course, was borne out by the fact that the specimens were extremely weak and broke upon machining. Upon sintering at 890°C., shrinkage occurred at all pressures. The 50-ton specimen showed a greater amount of shrinkage and the maximum sintered density was 8.16 (4 per cent porosity). It is interesting to note that the brass specimens all shrank on sintering, regardless of how high a pressure was used, whereas the copper specimens all expanded and blistered at high pressure.

Effect of Pressure on Hardness.—Fig. 14 shows that the hardness of the unsintered specimens increased with pressure to a maximum of Rockwell H-105 at 75 tons per sq. in. Higher pressure showed no increase in hardness, indicating that maximum cold-working of the compact was attained at 75 tons per sq. in. The specimens sintered at 650°C. all showed about 10 per cent decrease in hardness, while those sintered at 890°C. showed about 5 per cent decrease in hardness. This indicates that at 650°C. the compact is annealed and softens, while at 890°C. the annealed compact has also sintered and shrunk, which would tend to harden the compact, and that is the reason why the 890°C. specimens are harder than those sintered at 650°C.

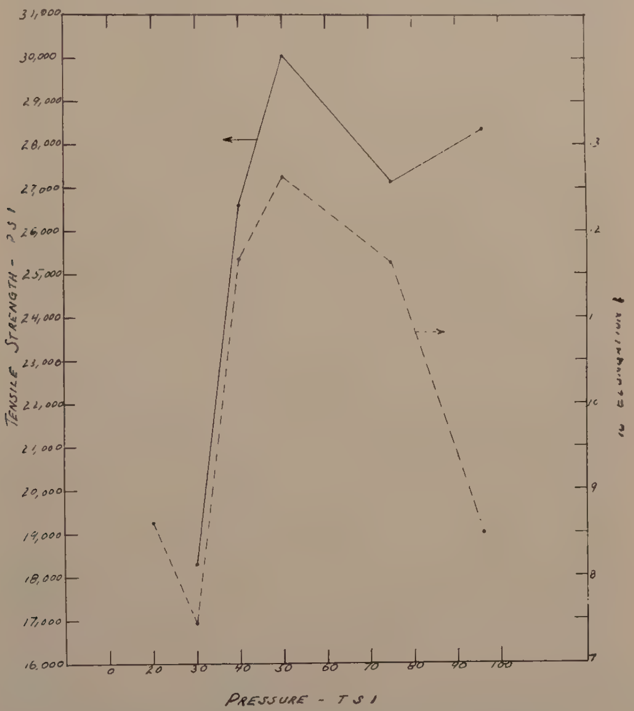

FIG. 15.—TENSILE STRENGTH VS. PRESSURE (SOLID LINE) AND PERCENTAGE OF ELONGATION VS. PRESSURE (DOTTED LINE) OF 70-30 BRASS POWDER.

Effect of Pressure on Tensile Strength and Percentage of Elongation.—Fig. 15 indicates that 50 tons per sq. in. is the optimum pressure to use for 70-30 atomized brass powder sintered at 890°C. At this pressure the maximum tensile strength (30,000 lb. per sq. in.) and the maximum elongation (12.6 per cent) were obtained. This checks work done at the New Jersey Zinc Company's laboratory, where investigators also found that the best physical properties on this powder are obtained when a pressure of 50 tons per sq. in. is used.

Effect of Pressure on Microstructure.—The structure of the original 70–30 brass powder is shown in Fig. 16. The particles have a dendritic structure typical of cast 70-30 brass and may contain traces of beta brass because of the extremely rapid cooling. Fig. 17 shows the microstructure of the 96-ton compact before sintering. The dendrites have been crushed and missaligned. Severe distortion (flattening) of the particles has taken place. Fig. 18 shows the structure of the 96-ton specimen after sintering at 890°C. Except for a certain amount of porosity, the structure of this specimen does not differ greatly from that of ordinary cold-worked annealed 70-30 brass. The beta phase has entirely disappeared and homogeneous alpha brass remains. The original particle boundaries are no longer visible. Recrystallization and twinning have taken place.

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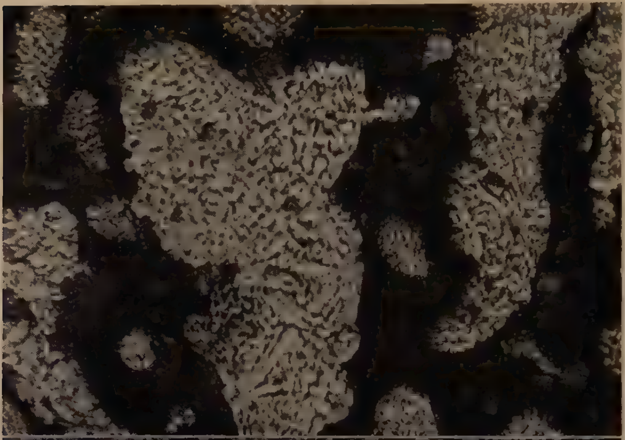

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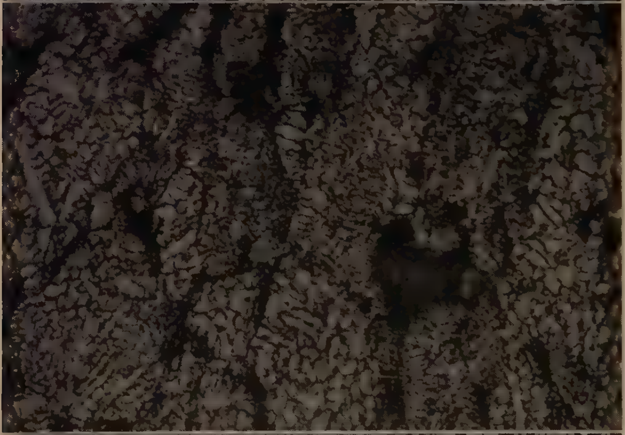

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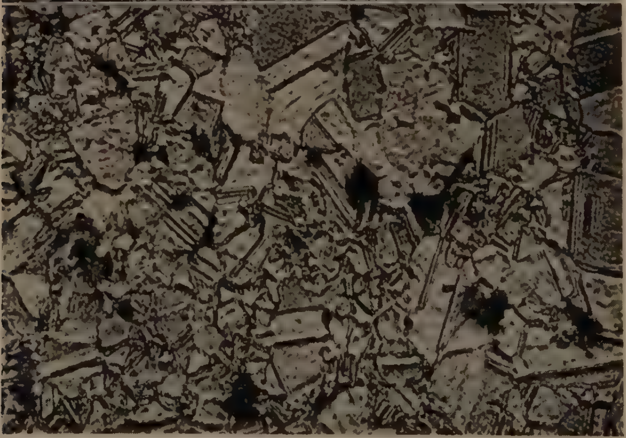


Fig. 16.—70-30 brass powder. Etchant NH_4OH and H_2O_2. × 500.

Fig. 17.—70-30 brass powder pressed at 96 tons per square inch, unsintered. Etchant NH_4OH and H_2O_2.

Fig. 18.—70-30 brass powder pressed at 96 tons per square inch, sintered at 890°C. Etchant NH_4OH and H_2O_2. × 500.

Conclusions.—From the work on brass, the following general conclusions can be drawn:

1. The optimum molding pressure to use for atomized 70-30 brass powder is 50 tons per sq. in. At this pressure, the best physical properties are secured for short time sintering.

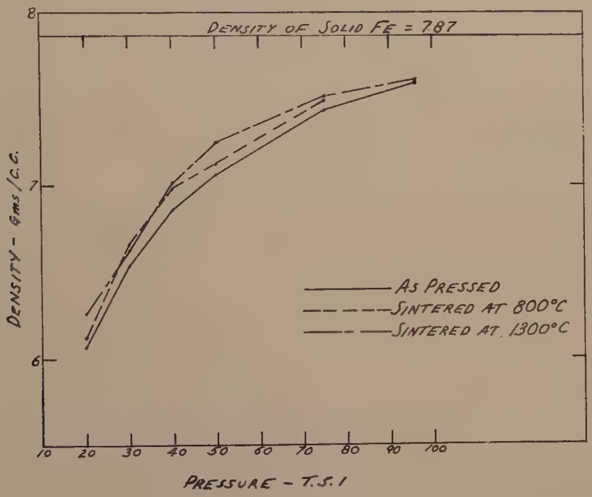


FIG. 19.—DENSITY VS. PRESSURE OF ELECTROLYTIC IRON POWDER.

2. It is necessary to sinter brass compacts close to their melting point to secure good physical properties (about 900°C. for 70-30 brass.)

3. Proper selection of molding pressure, sintering time and temperature results in brass compacts having good physical properties and microstructure, resembling those of ordinary wrought, annealed brass.

4. The application of excessive pressure in molding brass powder leads to poorer physical properties after sintering, probably because of excessive grain growth.

IRON

Effect of Pressure on Density.—Fig. 19 shows that the density of the unsintered specimens increases steadily with pressure to a maximum of 7.60 at 96 tons per sq. in., which corresponds to a porosity of 2 per cent. The densities after sintering at both 800°C. and 1300°C. show a slight increase; i.e., slight shrinkage. The densities are practically the same for both sintering temperatures, which indicates that the use of very high temperatures for electrolytic iron powder does not have much effect on the sintering of the material.

Effect of Pressure on Hardness.—Fig. 20 shows that the unsintered hardness closely follows the density curve, reaching a maximum of 116 at 96 tons per sq. in. The hardness after sintering was lower than for the unsintered compacts and was almost identical whether the 800°C. or 1300°C. sintering temperature was used.

Effect of Pressure on Tensile Strength.—Fig. 21 shows that sintering temperature does not have very much effect on the tensile strength of compacts of electrolytic iron powder. The two tensile-strength curves continually overlap each other. The tensile strength does increase with increasing pressure, and it is interesting to note that the highest tensiles at 96 tons per sq. in. are higher than the accepted values for massive pure iron. The tensile strength of the 96-ton specimens average about 43,000 lb. per sq. in., and the accepted value for pure Armco iron is 35,000 to 40,000 lb. per sq. inch.

Effect of Pressure on Percentage of Elongation.—Fig. 22 shows that temperature is

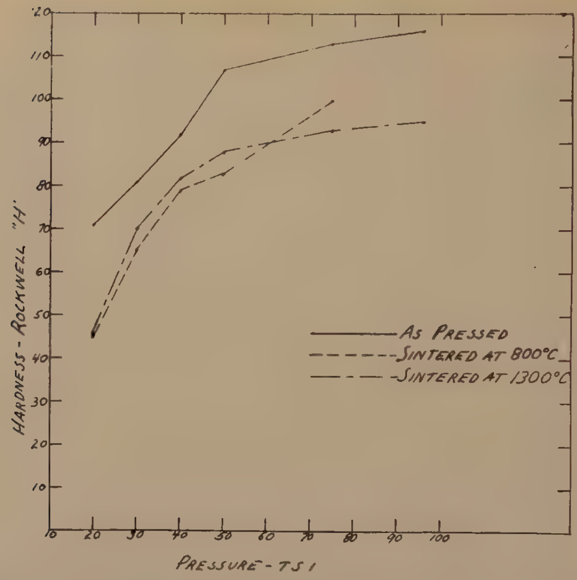


FIG. 20.—HARDNESS VS. PRESSURE OF ELECTROLYTIC IRON POWDER.

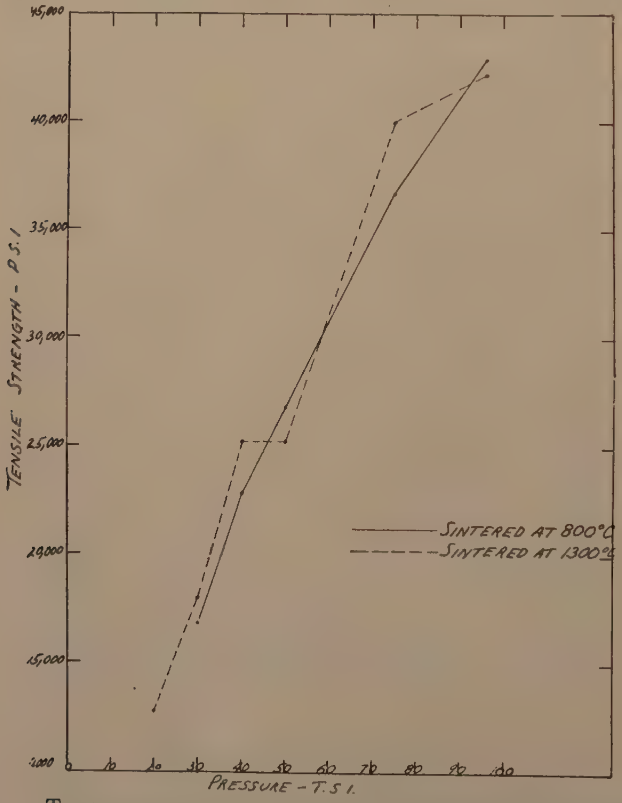


FIG. 21.—TENSILE STRENGTH VS. PRESSURE OF ELECTROLYTIC IRON POWDER.

important as far as ductility of sintered electrolytic iron is concerned. The specimens sintered at 1300°C. show greater increases in percentage of elongation at the higher pressures, while those sintered at 800°C. do not have such high elongations. Since the more highly pressed electrolytic iron specimens sintered at 1300°C. seemed to show remarkable ductility, the writer decided to check the percentage of elongation more accurately by machining dumbbell-shaped tensile specimens from some duplicate 2 by ½-in. rectangular blocks. These specimens were broken on the tensile-test machine and the percentage of elongation was calculated.

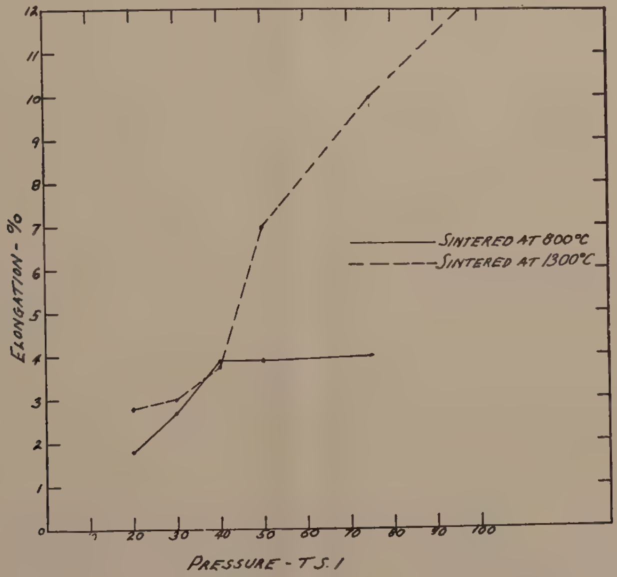


FIG. 22.—PER CENT ELONGATION VS. PRESSURE OF ELECTROLYTIC IRON POWDER.

Since all of the elongation occurred in less than one inch length, as indicated by the length between one-inch bench marks that were made on the sample, it was calculated on this basis. Several test pieces checked in this manner showed elongation of 50 to 55 per cent per inch. Fig. 23 shows the original test piece before machining and a test piece after machining and breaking. A comparison of the broken test piece with the scale in the photograph will verify the statement that elongation is about 55 per cent per inch.

Another 2 by ½-in. test piece 0.200 in. thick was cold-rolled down to a ribbon about 0.003 in. thick without any intermediate annealing. The thin ribbon still showed considerable ductility.

Effect of Pressure on Microstructure.—Fig. 25 shows that some distortion of the powder occurs at 50 tons pressure and Fig. 26 shows that at 96 tons considerable distortion and flattening of the particles has occurred, resulting in an alignment of the flat particles perpendicular to the direction of pressure.

Fig. 27 shows that a sintering temperature of 800°C. is sufficient to cause complete recrystallization of electrolytic iron compacts. This 50-ton specimen now has a rather fine grain structure and there is still some evidence of the original alignment of the particles. Comparison of Fig. 28 with Fig. 27 reveals that at 1300°C. considerable grain growth has occurred on the 50-ton specimens, resulting in a uniform polyhedral grain structure with all signs of particle alignment obliterated.

A comparison of Fig. 28 with Fig. 29 indicates that the original particle size of electrolytic iron powder has little or no effect on the final grain size of the sintered compact. Both these specimens were pressed and sintered under identical conditions but the sample shown in Fig. 29 was made using 325-mesh electrolytic iron powder whereas the sample of Fig. 28 was made using 100-mesh electrolytic iron powder. The grain size is about the same in both specimens. If there is any slight difference, it appears that the specimen of fine powder has somewhat larger grains. This may be caused by the fine particles being work-hardened throughout their entire cross section on pressing, leading to

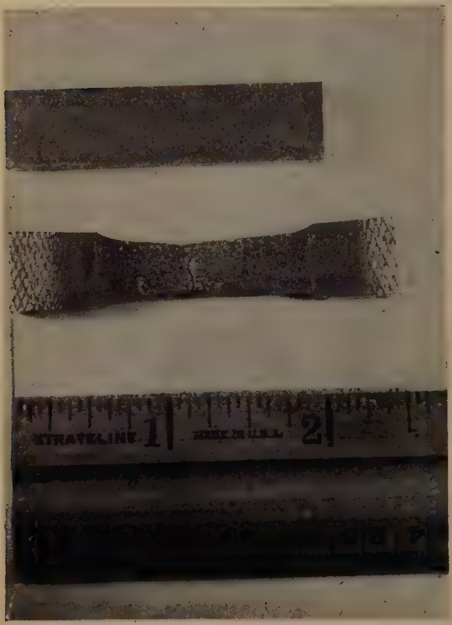
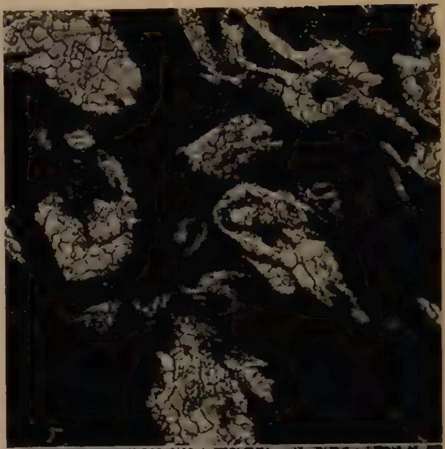


FIG. 23.—ORIGINAL TEST PIECE BEFORE MACHINING AND A TEST PIECE AFTER MACHINING AND BREAKING.



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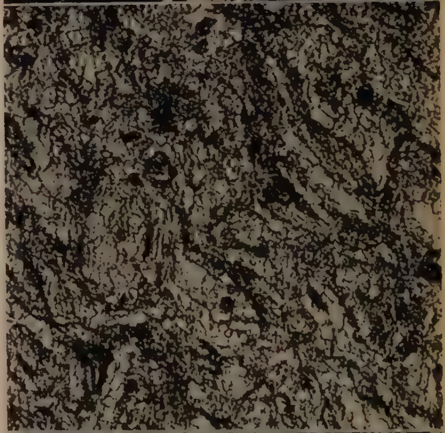

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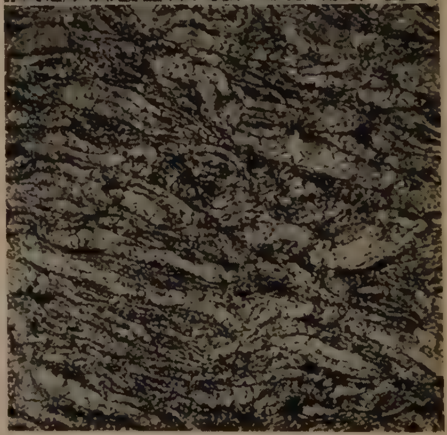

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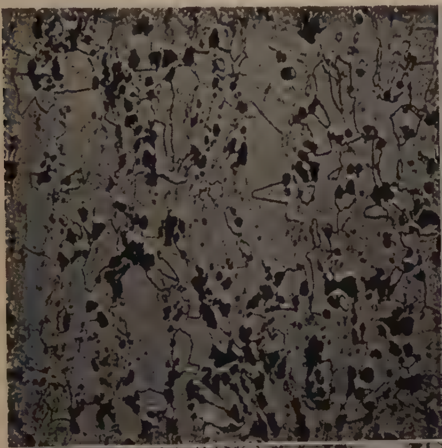
FIG. 24.—100-MESH IRON POWDER. ETCHANT 2 PER CENT NITAL. × 200.

FIG. 25.—IRON POWDER PRESSED AT 50 TONS PER SQUARE INCH. ETCHANT 2 PER CENT NITAL, UNSINTERED × 200.

FIG. 26.—IRON POWDER PRESSED AT 96 TONS PER SQUARE INCH. ETCHANT 2 PER CENT NITAL, UNSINTERED. × 200.

lower recrystallization temperature and therefore greater grain growth at the sintering temperature. The coarse powder particles probably are not work-hardened throughout their entire cross section because of the greater mass that must be deformed. The only apparent appreciable difference between these two specimens is that the one made of coarse powder has fewer and larger pores than the one made of fine powder.

A comparison of Fig. 28 with Fig. 30 reveals that the greater work-hardening caused by higher molding pressure causes a larger sintered grain size. Both these specimens were sintered one hour at 1300°C., but the one shown in Fig. 30 was subjected to twice the molding pressure of the specimen shown in Fig. 28 and has a grain size about twice the diameter of the latter. Many of these grains have grown around oxide inclusions, so that the inclusions are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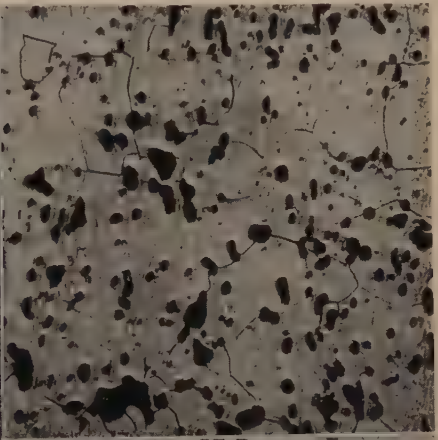
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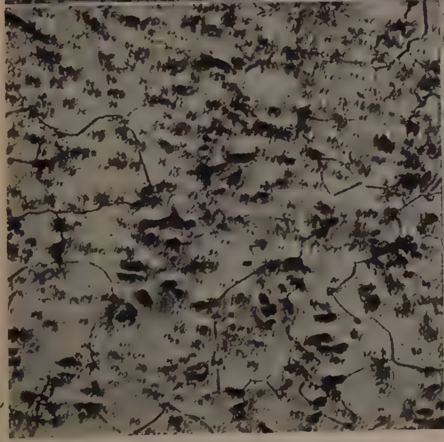
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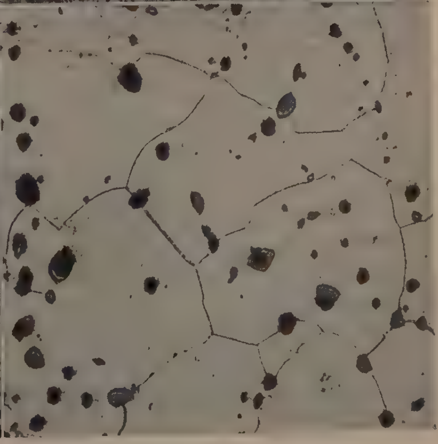
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FIG. 27.—100-MESH IRON POWDER PRESSED AT 50 TONS PER SQUARE INCH, SINTERED AT 800°C. ETCHANT 2 PER CENT NITAL. × 200.

FIG. 28.—100-MESH IRON POWDER PRESSED AT 50 TONS PER SQUARE INCH, SINTERED AT 1300°C. ETCHANT 2 PER CENT NITAL. × 200.

FIG. 29.—325-MESH IRON POWDER PRESSED AT 50 TONS PER SQUARE INCH, SINTERED AT 1300°C. ETCHANT 2 PER CENT NITAL. × 200.

FIG. 30.—100-MESH IRON POWDER PRESSED AT 96 TONS PER SQUARE INCH, SINTERED AT 1300°C. ETCHANT 2 PER CENT NITAL. × 200.

contained within the grain rather than at the grain boundary. This ability to grow around inclusions probably accounts for the excellent ductility of this material as previously described.

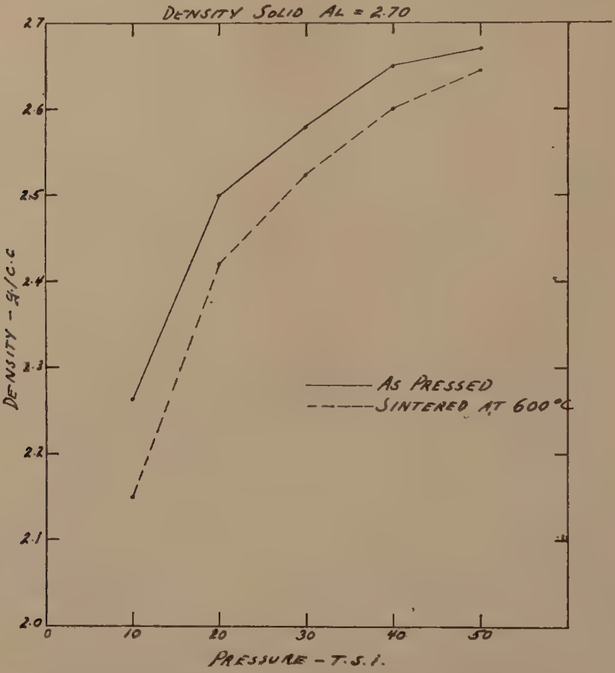

FIG. 31.—PRESSURE VS. DENSITY OF ALUMINUM POWDER.

Conclusions.—The following general conclusions can be drawn from the work done on electrolytic iron powder:

1. Higher molding pressure is necessary to achieve the best physical properties in electrolytic iron compacts sintered for one hour.

2. Sintering temperature does not have much effect on tensile strength or hardness, but a high sintering temperature is desirable where great ductility is required.

3. By the use of high pressure and high sintering temperature, it is possible to make sintered electrolytic iron compacts that give greater strength and ductility than pure massive iron.

4. The original particle size of the powder apparently has little effect on the grain size of the sintered specimen up to 325-mesh, although this may not be true of powder of still finer mesh.

5. Grain growth is accelerated by the use of high sintering temperatures and also by the use of high molding pressures.

6. When grain growth occurs, it tends to surround oxide inclusions so that they are located within the grains rather than at the grain boundaries.

ALUMINUM

Effect of Pressure on Density.—Fig. 31 shows that the density of compressed unsintered aluminum powder increases rapidly with increase in pressure throughout the pressure range used. The porosity of the unsintered aluminum was 1.11 per cent at the maximum pressure of 50 tons per sq. in. The densities after sintering were all lower than the unsintered densities, indicating that expansion occurred for all pressures. The amount of expansion appeared to decrease with increasing pressure, being a minimum at the highest pressure of 50 tons per sq. in. This is exactly opposite to the usual trend of metal-powder compacts. The writer feels that this phenomenon occurs because it is extremely important that the refractory oxide film on aluminum powder be removed in order to secure good adhesion between the particles, and that high pressures are necessary to push aside this oxide film. Consequently, good metal to metal contact and good sintering, with its accompanying shrinkage effects, is accomplished only with highly compressed specimens. With specimens pressed at lower pressures, the oxide film probably is not removed to a great extent, resulting in only slight sintering, in which case the expanding effects of included gases is a greater factor than the shrinkage effect of sintering forces.

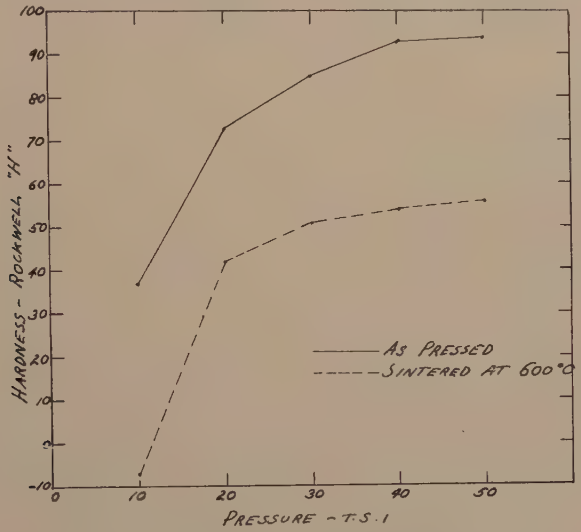

FIG. 32.—PRESSURE VS. HARDNESS OF ALUMINUM POWDER.

Effect of Pressure on Hardness.—Fig. 32 shows that hardness increases with pressure for both the unsintered and sintered specimens, the hardness tapering off between 40 and 50 tons per sq. in. All the sintered specimens are considerably softer than the unsintered, and the degree of softening is about the same in all, regardless of the pressure used. Apparently this indicates that the annealing effect of sintering is a greater factor in the hardness of sintered aluminum than the hardness effect of shrinkage forces during sintering.

Effect of Pressure on Tensile Strength.—Fig. 33 shows that the tensile strength of the sintered aluminum compacts increased rapidly with pressure to a maximum of 13,500 lb. per sq. in. at the maximum pressure of 50 tons per sq. in. This is exactly the result one would expect, since the tensile strength normally would follow the density curve.

Effect of Pressure on Percentage of Elongation.—Fig. 33 also shows that the maxmum elongation of 5 per cent occurs at the pressure of 40 tons per sq. in. and the elongation drops off at the highest pressure of 50 tons per sq. in. The drop in elongation at the highest pressure may be due to an experimental error, since in all the other specimens the elongation curve followed the tensile curve.

Great difficulty was experienced in preparing etched sintered aluminum specimens, therefore no photomicrographs were made.

Conclusions.—From the work on aluminum powder, the following general conclusions can be drawn:

1. The physical properties of aluminum compacts, such as density, strength and ductility, increase with increasing pressure up to the practicable pressure limits.

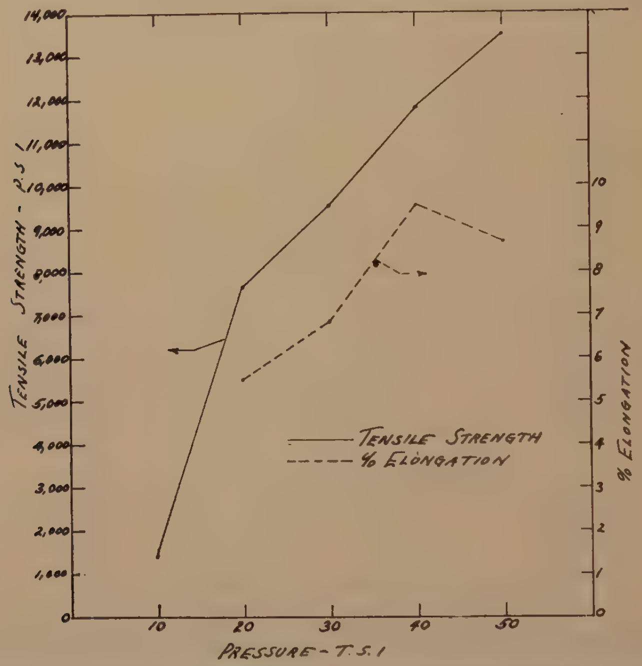

FIG. 33.—TENSILE STRENGTH AND PERCENTAGE OF ELONGATION VS. PRESSURE OF ALUMINUM POWDER.

2. Good properties in aluminum compacts can be secured only by the use of high pressures, because it is necessary to rupture the refractory oxide film on aluminum powder.

3. Considerable softening of the specimens occurs upon sintering, regardless of the pressure used.

GENERAL CONCLUSIONS

1. For relatively short-time sintering, molding pressure is a very important factor in the final physical properties of the sintered specimens.

2. The effect of pressure is different for each metal, so that few general rules can be drawn that would apply to all metals.

3. In many cases, for a particular metal powder and sintering temperature, there is a critical pressure at which the best physical properties can be obtained.

4. The principles of cold work and annealing and their effect on grain structure applied to massive metal also holds true for sintered metals.

5. Particle size, at least for electrolytic iron powder, does not have a great effect on ultimate grain size.

DISCUSSION

(*E. E. Schumacher presiding*)

E. V. CRANE.*—I was particularly impressed with Dr. Kuzmick's work on tin. Is not the illustration, particularly the second one, a very good illustration of hot pressing, in that the tin recrystallizes below room temperatures and the heat generated in the compression would bring it further up in its recrystallization range?

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* E. W. Bliss Co., Brooklyn, N. Y.

J. F. **Kuzmick**.—Yes. I think that is a very interesting point. We might paradoxically state that in cold-pressing tin powder we are also hot-pressing tin powder, since recrystallization occurs below room temperature. Therefore the results we achieved in cold-pressing tin powder are about what we might expect if we hot-pressed other metal powders having higher recrystallization temperatures.

E. V. **Crane**.—One more. I did not note particularly the effect in the aluminum, but I note that in the cold-pressing of aluminum we do create enough heat in the cold-pressing process to bring out a resultant material that is not severely cold-worked; that is, there is enough heat generated to be up close to the recrystallization range. Did you observe anything of the sort in the aluminum pressing?

J. F. **Kuzmick**.—No, I had not observed any generation of heat that would bring it up to such a temperature, although this was done under laboratory conditions, operating at a very slow rate and with a hand-operated hydraulic press. Perhaps in a high-speed press such a condition would obtain.

F. V. **Lenel**.—Dr. Kuzmick's curves for electrolytic iron powder and aluminum powder show that with increasing pressure, sintered density, hardness, tensile strength, and ductility also increase. On the other hand, the curves for copper powder show a maximum in these properties at a critical pressure and a falling off at higher briquetting pressures; the curves for brass powder show steadily increasing sintered density and hardness with increasing briquetting pressure but a maximum in tensile strength and ductility. The question arises, what causes this difference in the character of the curves? I wonder whether the conditions of sintering may not be responsible rather than any pecularity in the structures of the metals themselves.

Nothing is said in Dr. Kuzmick's paper about the rate at which the compacts were heated to the sintering temperature. Observations we have made confirm those of Mr. Kalischer (p. 579) that expansion on sintering can be overcome by a sufficiently slow rate of heating, which allows adsorbed or dissolved gases and gases developed by reactions taking place during sintering to escape. It seems certain that such gases, in particular water vapor, are responsible for the expansion of the copper compacts that were briquetted at high pressure, and that the blistering and swelling is due to a phenomenon analogous to the hydrogen embrittlement of cast or wrought copper containing cuprous oxide as impurity, when it is heated in hydrogen.

Why the strength and ductility of sintered brass-powder compacts fall off with increasing briquetting pressures cannot be decided on the basis of Dr. Kuzmick's data. It would be interesting to investigate further whether this falling off is also due to the effects of extraneous materials like gases, or to reactions taking place in the metal itself, such as homogenization or grain growth.

J. F. **Kuzmick**.—In regard to the expansion of sintered copper compacts that have been subjected to high molding pressure, the heating rate applied to the original specimens was one that would be encountered in normal practice. It took about 15 min. for the specimens to come up from room temperature to sintering temperature. However, I have since run some similar copper compacts using a very slow heating rate, taking as long as 4 hr. to reach sintering temperature from room temperature, and found no change at all. The compacts molded at high pressure still blistered and expanded considerably even with the slow heating rate.

Reduced copper powder was the worst in this respect, while electrolytic copper powder was considerably better. I am now running some tests on atomized copper powder and the indications so far are that this material will not blister and expand at all when high pressures are used. Apparently the porosity of the powder particles has a great deal to do with this effect.

I have not arrived at any definite conclusions as to why the sintered brass-powder compacts fell off in physical properties with briquetting pressures over 50 tons per sq. in. It may be that the beneficial effects of greater density and hardness with increasing pressure are more than counteracted by the deleterious effect of reactions such as grain growth. The New Jersey Zinc Co., which manufactures the brass powder I used, recommends 50 tons per sq. in. as the optimum molding pressure. This would tend to corroborate my findings.

In a paper the length of mine, I could not very well go into all these details. Furthermore, this is a project on which I am continuing to work whenever I have time, therefore my findings are not yet finished. The paper I presented, as its title implies, merely gives the results on experiments I had conducted up to the time the paper was presented.

C. G. Goetzel.—Referring to the same subject of tin, I would like to bring out the problem of the oxygen coats found on tin and lead powders, which tend to prevent the diffusion of the individual particles into a solid structure. Tin oxide can be reduced only at a temperature above the melting point of tin. When pressing this highly plastic powdered mater al with some of the nonremovable oxide coats, there is reason to believe that most of the oxide skins are not disturbed and consequently the union of the particles is rather weak. It has been found, however, that both tin and lead powders pressed at high pressures, say from 30 to 80 tons per sq. in., could be consolidated to such an extent that they could be subjected to cold-rolling into sheets without any heat-treatment. On the other hand, if heat-treatment was carried out either in air or in hydrogen, or in carbon monoxide, the ductility and malleability of the compacts were greatly impaired and far below in comparison with the compacted powders.

J. F. Kuzmick.—I cannot add many comments to that statement, since I have not tried heat-treating the tin specimens. Also, because of the extremely fine particle size, it was difficult to observe what happened to the oxide film under the microscope.

GENERAL DISCUSSION

E. E. Schumacher presiding

C. W. Balke.*—In listening to these papers I am impressed by the fact that, while a number of the authors indicate that they recognize that oxygen is present on the surface of the metal particles, they do not tell us how much oxygen was present in any of the powders used in the experiments. Last year I gave a paper on the effect of pressure on the properties of compacts. The results obtained while working with four different electrolytic iron powders were presented and in each case the exact hydrogen loss of each powder was given.

The compacts made from iron powders as described in the last paper were not prepared with pressures sufficiently high to prevent the removal of oxygen by sintering in hydrogen. A compact pressed at 160 tons per sq. in., and from an iron powder containing 0.5 per cent of oxygen, retains a large part of that oxygen after sintering, and its properties are quite different from those of a similar compact made from an iron powder containing 0.002 per cent of oxygen. Using this low-oxygen-content powder, sintered compacts were obtained having tensile strengths as high as 60,000 lb. per sq. in. and with other physical properties superior to those of ingot iron. Iron powder of this quality can be pressed to a density of 7.86, or practically solid iron. This is also true of the tin mentioned in one of the papers. In such cases any oxide present in or on the metal particles will become locked inside the compact and is not likely to be removed during sintering. The presence of this oxide will have an effect on the properties of the finished product. Even in tantalum the oxide must be eliminated or the metal will not exhibit its maximum softness and ductility.

I wish to take this opportunity to urge that we fully recognize that oxygen is an impurity in many metal powders, and that the amount present in powders used in experimental work be determined and stated. This will make it possible to compare more intelligently the results of different investigators.

J. F. Kuzmick.—I heard Dr. Balke's excellent paper that he has just mentioned, and I agree with him 100 per cent that it is very important to know how much oxygen is in a powder. However, we cannot do everything all at once, and in this particular case we just took typical molding powders that are on the market. We did know how much oxygen was present, but in order to present the material I wanted I neglected to include those figures.

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* Fansteel Metallurgical Corporation, North Chicago, Illinois.

The iron powder used was a standard ground of electrolytic iron powder, and hydrogen loss ran approximately 0.5 per cent.

As far as the loss of oxygen during sintering, or reduction of oxide film, I merely pointed out observations that I made, and evolved the theory that complete reduction did not occur because the dense specimens did not allow penetration of the hydrogen to all the oxide inclusions. However, if he finds other results, that is something we would like to know about.

G. J. Brittingham.*—I would like first to take the opportunity to say thank you for the privilege of coming here and listening to these papers. But there are a few things on which I would like a little more information. One is in connection with the brass powder Dr. Kuzmick referred to. I understand that it was an atomized powder and that he did not get sintering at relatively high temperatures, 650° I think was the temperature mentioned. Unfortunately, it has been my job in Australia to try to produce copper powder, and when we produce copper powder, and from the studies that we have made in connection with it, we know very well that sintering of copper does occur at temperatures very much lower than 650° when the copper is free of oxide on the surface.

I think there is not any question of oxide, and the amount of oxide and the distribution of the oxide is a very important matter. I think we should always keep in mind the point that the results we obtain sometimes will not fit in with what we think they should be but the explanation should be sought after rather than to make the results fit in.

I feel certain that it might not have been possible to completely oxidize that brass powder before pressing, but had that been done I feel very certain that sintering would have commenced at a very much lower temperature than 650°.

J. F. Kuzmick.—As far as the copper powder used in this experiment is concerned, since copper does oxidize very rapidly, the powder was freshly reduced in hydrogen immediately before pressing, and the specimens were sintered immediately after pressing, so that the oxide film was about as low as we could get it under the conditions in which we were working. Of course, we had an oxide film, because as soon as we took the powder out of the reduction furnace it undoubtedly oxidized to some extent.

C. J. Bier.—I should like to make a point here that ought to be stressed. There are two distinct types of oxides in metal powders; the internal oxide and the external oxide. It is not only important that the powder fabricator know the oxide contents of the powder but also that he study the position of the oxide. The atmosphere used in sintering is just as important in the sintering reaction as the oxide contents.

C. G. Goetzel.—I want to discuss the second part of the question; namely, the fatigue properties of metal powders. To date relatively little work has been done on fatigue. All that is known is that the values are surprisingly favorable even in compacts that have a high degree of porosity. The fatigue value is relatively high, comparing favorably with the same value for bulk materials of customary tensile strengths. The work so far has been concentrated on copper and iron compacts, two rather ductile metals, and little is known about steel and alloys that may be somewhat more brittle, giving perhaps lower fatigue data. I think there is quite a field for research.

I should like to bring one other question up here, and that refers to oxygen. How can we get commercial powders that have less oxygen? How can we get them in sufficient quantities? And, if that is not possible, how can we purify them on a commercial scale to take advantage of the possibilities inherent in low-oxygen-content powders? Oxygen is just as bad in the form of films or of oxygen inclusions as in the form of solid oxygen particles, which sometimes are recognized in the reduced type of powder.

Question.—Is the reduction of copper oxide really effective at temperatures as low as 275°C.?

C. G. Goetzel.—The temperature used for purification of the powders was 275°C. Copper in previous work had been reduced at a temperature of 350°C. The reason the temperature was kept so low was that at higher temperatures the powder tends to agglomerate and sinter; it can be comminuted only by more or less severe work-hardening, which distorts the particles, causes stresses and may impair the compressibility of the powders.

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* Superintendent, Electrolytic Refining and Smelting Corporation of Australia, Port Kembla, N. S. W., Australia.

The oxygen content of the powders used in this work was relatively low, being in the order of one tenth of one per cent, since both metals were electrolytic powders. It may be assumed that part of the oxygen was present in the form of surface films, especially in tin, for which the 325-mesh powder was used.

The powders thus cleaned were kept at the temperature of 275° for one hour. This temperature was selected on the basis of some practical experiments and was believed to be sufficient to reduce most of these oxide films.

Another point to be considered, was that these powders, because of their large surface, had a tendency to absorb gases, especially hydrogen, and that during compacting and, afterward, during sintering peculiar phenomena occur which are generally known as hydrogen embrittlement. To eliminate the hydrogenization of these particles as much as possible, the vacuum treatment was added to the regular reduction cycle. This vacuum treatment may have contributed largely to the fact that in sintering shrinkage occurred instead of growth caused by possible gas inclusions.

G. J. Brittingham.—If I might say a word regarding this production of low oxygen content in copper powder. We have had to work from first principles in regard to production of powders and consequently we have come to this problem from perhaps a somewhat different aspect from those of you who are working on the matter here today. Naturally any producer of raw material will have complaints from the fabricator of that raw material and we had that experience. We were told, amongst other things, "Your oxygen content is too high." We set about trying to reduce that oxygen content and maintain it at the low figure. When I say maintain it at the low figure, I mean this: We are situated actually 600 miles from the fabricating plant, so that there is ample time for absorption of oxygen by the material after production. And that is a point that I think cannot be overstressed, that these powders, by reason of their excessive surface in comparison with their mass, are subject to very rapid pickup—and just the complete rapidity of it is determined entirely by the nature of the surface. We are producing an electrolytic powder, which, as you know, is dendritic in nature, and there is a very high surface in regard to mass.

That point brings us to the greatest difficulty, that of keeping the oxygen down. There are certain points to be considered: you can modify that structure, that appearance, that actual surface prior to finishing (with the powder) the production process, and by that modification we can actually get that oxygen content down very very low in the powder as produced. We can actually pack it and transport it 600 miles, by sealing it in a tinplate container and soldering the container; with something like 0.05 per cent of oxygen as an upper limit. But that does not solve the problems completely because in altering the surface of the powder you have also altered some of the sintering properties of that powder, and the answer may not be to completely reduce the oxygen. It may be preferable to have the sintering conditions that are obtainable in the dendritic powder.

(The meeting adjourned at 5 p.m.)

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An Electrical Analogue of the Flow of Heat in a Regenerator System. By K. Heindlhofer and B. M. Larsen. (*Metals Technology*, August 1945) (With discussion)

A Completely Automatic Control of Open-hearth Reversal. By B. M. Larsen and W. E. Shenk. (*Metals Technology*, June 1945)

A Rapid Laboratory Method for Estimating the Basicity of Open-hearth Slags. By W. O. Philbrook, A. H. Jolly, Jr. and T. R. Henry. (*Metals Technology*, August 1945)

Application of pH Slag-basicity Measurements to Basic Open-hearth Phosphorus Control. By Michael Tenenbaum and C. C. Brown. (*Metals Technology*, August 1945) (With discussion)

Effect of Ingot Delivery Time as a Factor in Quality of Bessemer Steel. By Howard C. Dunkle. (*Metals Technology*, August 1945) (With discussion)

Structure and Properties of Iron-rich Alloys

Creep Properties of Some Binary Solid Solutions of Ferrite. By Charles R. Austin, C. R. St. John and R. W. Lindsay. (*Metals Technology*, August 1945)

Recovery of Cold-worked Aluminum Iron as Detected by Changes in Magnetic Properties. By J. K. Stanley. (*Metals Technology*, January 1945)

Effect of Variables on the Recrystallization of Silicon Ferrite in Terms of Nucleation and Growth. By James K. Stanley. (*Metals Technology*, August 1945) (With discussion)

Oxide-metal Layers Formed on Commercial Iron-silicon Alloys Exposed to High Temperatures. By Raymond Ward. (*Metals Technology*, August 1945)

The Liquidus-solidus Temperatures and Emissivities of Some Commercial Heat-resistant Alloys. By James T. Gow, Anton de S. Brasunas and Oscar E. Harder. (*Metals Technology*, August 1945) (With discussion)

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Transformation of Austenite

Transformation of Austenite in a Steel Containing 3 Per Cent Chromium and 1 Per Cent Carbon. By E. P. Klier. (*Metals Technology*, September 1945)

Isothermal Transformation of Austenite in One Per Cent Carbon, High-chromium Steels. By Taylor Lyman and Alexander R. Troiano. (*Metals Technology*, September 1945) (With discussion)

Time-temperature Relations in Tempering Steel. By J. H. Hollomon and L. D. Jaffe. (*Metals Technology*, September 1945) (With discussion)

Time-temperature Transformation Curves for Use in the Heat-treatment of Cast Steel. By C. T. Eddy, R. J. Marcotte and R. J. Smith. (*Metals Technology*, September 1945)

Properties and Structure of Steel

Tensile Deformation. By John H. Hollomon. (*Metals Technology*, June 1945) (With discussion)

Effects of Cold-rolling on the True Stress-strain Properties of a Low-carbon Steel. By F. J. Mehringer and C. W. MacGregor. (*Metals Technology*, September 1945)

Distribution of Carbon between Titanium and Iron in Steels. By W. P. Fishel and Brison Robertson. (*Metals Technology*, October 1944) (With discussion)

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A Modified Vacuum Extraction Apparatus. By W. D. Brown

Determination of Hydrogen by Vacuum Extraction and Tin Fusion. By John Naughton

Determining the Hydrogen Content of Molten Steel by Vacuum Extraction. By C. B. Post and D. G. Schoffstall

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